Depth-profiling of Surface Oxide Film/Metal Systems

By Masahiro Seo* and Norio Sato*

Depth-profiling of various surface oxide film/metal systems ($\text{Cr}_2\text{O}_3/\text{Cr}$, $\text{Fe}_2\text{O}_3/\text{Fe}$, NiO/Ni and $\text{Nb}_2\text{O}_5/\text{Nb}$) was performed with simultaneous use of Auger electron spectroscopy and argon-ion sputter-etching (1 kV , $4 \times 10^{-5}\text{ A} \cdot \text{cm}^{-2}$) to obtain fundamental knowledge necessary for quantitative analysis of steel surface layer in depth. The composition broadening at the film/metal interface was observed for all systems. The location of the film/metal interface, Z , and the depth-resolution, ΔZ , were determined by assuming that the composition broadening at the interface obeyed an error function.

The average sputtering rate, v , of surface oxide film was measured from a linear relation between the film thickness, L_f , ellipsometrically or coulometrically obtained and the location of the film/metal interface, Z , expressed in terms of sputtering time. The value of v decreased in the order of NiO (4.3 nm min^{-1}), Nb_2O_5 (4.0 nm min^{-1}), Fe_2O_3 (2.9 nm min^{-1}) and Cr_2O_3 (1.9 nm min^{-1}). The relative depth-resolution, $\Delta Z/Z$, plotted as a function of Z depended on the film/metal system and further, discussion was made on predominant factors influencing the depth-resolution.

(Received July 29, 1985)

Keywords: *depth-profile, sputter-etching, surface analysis, surface oxide film, Auger electron spectroscopy*

I. Introduction

Measurement of depth-composition profile of thin surface layer on solid is of particular importance for surface technology, micro-electronics, corrosion science and heterogeneous catalysis. Combination of surface analytical technique such as Auger electron spectroscopy (AES) with ion-sputtering has been widely used for the measurement of depth-composition profile. Ion-sputtering, however, is a destructive surface sectioning method which involves the factors⁽¹⁾⁽²⁾ altering the surface composition such as preferential sputtering, atomic mixing and surface roughening. These factors, therefore, must be taken into consideration for the quantification of sputtering-profiles. In addition to these factors, an accurate measurement of sputtering rate is indispensable for the quantification of depth-direction.

In steel industry it is a very serious problem to control surface properties of steels. Steel surfaces are always covered with oxide films. Although depth-profiling⁽³⁾⁻⁽⁷⁾ of surface oxide films on ferrous metals and steels has been per-

formed for surface characterization, there are few systematic studies on sputtering rates and sputtering process of surface oxide films.

In the present study, depth-profiling of various surface oxide film/ferrous metal systems was performed with simultaneous use of AES and argon-ion sputter-etching to obtain fundamental knowledge necessary for quantitative analysis of steel surface layer in depth.

II. Experimental

1. Preparation of surface oxide film/metal systems

Pure metallic plates ($0.2\text{ cm} \times 1.0\text{ cm} \times 2.0\text{ cm}$) of chromium, iron, nickel and niobium were used as substrate materials. Surface oxide films were prepared on the respective metallic plates with dry oxidation for chromium, iron and nickel, and with anodic oxidation for niobium. The plate specimens were polished on emery paper in steps down to No.2000, finally polished with $\alpha\text{-Al}_2\text{O}_3$ abrasives ($0.05\text{ }\mu\text{m}$) and washed with acetone using an ultrasonic technique. Dry oxidation was performed at 523–823 K for 15 min–90 min in pure oxygen gas at a pressure of $1.33 \times 10^4\text{ Pa}$ for preparation of surface oxide films with different

* Faculty of Engineering, Hokkaido University, Kita-13 Jo, Nishi-8 Chome, Kita-ku, Sapporo 060, Japan.

thicknesses, whereas anodic oxidation was performed in $1.0 \text{ mol} \cdot \text{dm}^{-3}$ phosphoric acid solution under a constant current density of $2 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2}$, followed by potentiostatic treatment for 30 min at a desired potential. The thickness of surface oxide films thus prepared with dry oxidation and anodic oxidation was measured by a multiple-angle-of-incidence ellipsometry⁽⁸⁾ in air after oxide formation and coulometry *in situ*, respectively.

2. Depth-profiling

An Auger apparatus (PHI, 540A) was used for the measurement of depth-composition profiles of the surface oxide film/metal systems. After exposure in air, the specimen was inserted into the Auger apparatus. The sputter-etching was performed at an argon pressure of $6.7 \times 10^{-3} \text{ Pa}$ by rastering an argon-ion beam of 1 kV and $4 \times 10^{-5} \text{ A} \cdot \text{cm}^{-2}$ with a diameter of about 2 mm on a surface area of $6 \text{ mm} \times 6 \text{ mm}$. The relative angle of the argon-ion beam to the specimen was about 80° . Auger spectra were taken by using the primary electron beam of 3 kV, about $5 \mu\text{A}$ and a modulation voltage of 4 V and 30 kHz. The primary electron beam with a diameter of about $50 \mu\text{m}$ was aligned to the center of the specimen area sputtered by the argon-ion beam.

III. Results and Discussion

1. Typical depth-profiles of surface oxide/metal systems

Typical depth-profiles of the surface oxide film/metal systems are shown in Figs. 1–4, where the Auger peak-to-peak height (pph) ratios of oxygen (510 eV) to metallic components, Nb(197 eV), Cr(529 eV), Fe(651 eV) and Ni(848 eV) are plotted as a function of sputtering time. There was no significant carbon contamination on the uppermost surface of the respective oxide film. The depth-profiles are divided into three regions: In the initial zone, the pph ratio of O/Me decreases rapidly with sputtering time due mainly to preferential sputtering of oxygen component. Afterwards, a dynamic steady-state characterized by a constant pph ratio of O/Me is achieved, in which

Fig. 1 Typical depth-profile of $\text{Nb}_2\text{O}_5/\text{Nb}$ system.

Fig. 2 Typical depth-profile of $\text{Cr}_2\text{O}_3/\text{Cr}$ system.

Fig. 3 Typical depth-profile of $\text{Fe}_2\text{O}_3/\text{Fe}$ system. Fig. 4 Typical depth-profile of NiO/Ni system.

oxygen and metal components are sputtered in the proportion of the bulk film composition. Finally, the sputter-etching attains the film/

metal interface and hence, the pph ratio of O/Me decreases again with sputtering time.

2. Determination of the film/metal interface

Even if the composition at the film/metal interface is sharp just like a step-function as shown schematically in Fig. 5, ion-sputtering induces the composition broadening at the interface. In the case where the composition broadening at the interface obeys an error function, the position of the interface, Z , can be determined by the procedure depicted in Fig. 5. An error function is characterized by the standard deviation, σ . The depth resolution⁽¹⁾, ΔZ , therefore, will be defined by the 2σ values which correspond to the duration of the sputtering time between 86% and 14% of a constant composition ratio, O/Me , of the film. As depicted in Fig. 1–Fig. 3, the location of the interface, Z , is determined by the same procedure as in Fig. 5, assuming an error function like a distribution at the interface of the film/metal systems except for the NiO/Ni system. The composition broadening at the interface of the NiO/Ni system rather obeys an exponential function as shown by the dotted line in Fig. 4 and hence, the position of the NiO/Ni interface is defined by the sputtering time, Z , corresponding to a reciprocal of exponent in the composition ratio curve.

Fig. 5 Schematic depth-profile of MeO/Me system for definition of location of film/metal interface, Z , and of depth-resolution, ΔZ .

3. Average sputtering rates of surface oxide films

Figures 6–9 show the relation between the film thickness, L_f , ellipsometrically or coulometrically obtained and the location of the interface, Z , expressed in terms of sputtering time for the respective film/metal system. From these figures it is seen that a good linear relationship holds between Z and L_f . The average sputtering rate of the oxide film can be obtained from the slope of the linear line. The average sputtering rate of the oxide film thus obtained was listed in the first column of Table 1. In the second column of Table 1, the sputtering rate of the respective film was converted into the sputtering yield, $Y(\text{atoms ion}^{-1})$ by using the following equation⁽⁹⁾,

$$Y = \frac{v \cdot \rho \cdot F}{\bar{M} \cdot j_p}, \quad (1)$$

where v is the sputtering rate of the film ($\text{cm} \cdot \text{s}^{-1}$), ρ the density of the film ($\text{g} \cdot \text{cm}^{-3}$), F the Faraday constant, $\bar{M}$ the mean atomic weight of the film (for example, $\bar{M} = M(\text{Cr}_2\text{O}_3)/5$ for Cr_2O_3 film) and j_p the current density ($\text{A} \cdot \text{cm}^{-2}$) of argon-ion beam. The sputtering yield, Y , of the iron oxide film was calculated for the two possible types of oxide films, Fe_2O_3 and Fe_3O_4 , formed on iron under the preparation condition of the films.

Fig. 6 Relation between film thickness, L_f , coulometrically obtained and location of $\text{Nb}_2\text{O}_5/\text{Nb}$ interface, Z , expressed in terms of sputtering time. Q_T : electric charge required for formation of anodic oxide film.

Fig. 7 Relation between film thickness, L_f , ellipsometrically obtained and location of $\text{Cr}_2\text{O}_3/\text{Cr}$ interface, Z , expressed in terms of sputtering time.

Fig. 8 Relation between film thickness, L_f , ellipsometrically obtained and location of $\text{Fe}_2\text{O}_3/\text{Fe}$ interface, Z , expressed in terms of sputtering time.

Fig. 9 Relation between film thickness, L_f , ellipsometrically obtained and location of NiO/Ni interface, Z , expressed in terms of sputtering time.

Table 1 Sputtering Rate, v , and Sputtering Yield, Y of Surface Oxide Film

	$v/\text{nm} \cdot \text{min}^{-1}$	$Y/\text{atoms} \cdot \text{ion}^{-1}$
NiO	4.30	3.20
Nb ₂ O ₅	3.95	1.82
Fe ₂ O ₃ /Fe ₃ O ₄	2.87	1.86/1.80
Cr ₂ O ₃	1.93	1.33

4. Relative depth-resolution, $\Delta Z/Z$, of the film/metal system

The relative depth-resolution of the film/metal system defined by $\Delta Z/Z$ was plotted as a function of Z in Fig. 10. The NiO/Ni system is excluded from Fig. 10, since the relative depth-resolution, $\Delta Z/Z$, is nearly 100% irrespective of Z . The relative depth-resolution, $\Delta Z/Z$, depends on the system and improves in the order of the NiO/Ni, Fe₂O₃/Fe, Cr₂O₃/Cr and Nb₂O₅/Nb systems. There are many factors⁽¹⁾⁽²⁾ influencing the depth-resolution such as initial

surface roughness⁽¹⁰⁾, statistical nature of sputtering⁽¹¹⁾, crystal orientation⁽¹²⁾, preferential sputtering⁽¹³⁾, atomic mixing⁽¹⁴⁾ or knock-on effect.

If each factor contributes separately to the composition broadening at the interface, the total depth-resolution, ΔZ_T , is given⁽¹⁵⁾ by

$$\Delta Z_T = [\sum_i (\Delta Z_i^2)]^{1/2}, \quad (2)$$

where ΔZ_i is the contribution of each factor to depth-resolution. Hofmann⁽¹⁾ has interpreted the factors contributing to depth resolution. The initial surface roughness and the surface roughening due to statistical nature of sputtering provide the relative depth-resolution, $\Delta Z/Z$, proportional to $Z^{-1/2}$, whereas the crystal orientation and imperfections lead to the constant value of $\Delta Z/Z$ irrespective of Z . Besides, preferential sputtering, atomic mixing or knock-on effect gives the relative depth-resolution, $\Delta Z/Z$, proportional to Z^{-1} . The predominant factors influencing the depth-resolution, therefore, would be evaluated from the slope of linear line in Fig. 10. The formation of oxide islands provides the increase of initial surface roughness. From the surface observation of the oxide films by a scanning electron microscope, it was found that the surface roughness decreased in the order of the Fe₂O₃/Fe, NiO/Ni, Cr₂O₃/Cr and Nb₂O₅/Nb system. The exceptional composition broadening of the NiO/Ni system may be ascribed partly to the actual concentration gradient⁽⁴⁾. At present, however, quantitative evaluation of individual factor influencing the depth-resolution encounters difficulties, because combination of the factors gives complicated contribution. Further studies on depth-profiling of surface oxide films, therefore, are necessary to understand the composition broadening at the film/metal interface.

IV. Summary

Depth-profiling of various surface oxide film/metal systems (Cr₂O₃/Cr, Fe₂O₃/Fe, NiO/Ni and Nb₂O₅/Nb) was performed with simultaneous use of Auger electron spectroscopy and argon-ion sputter-etching. The composition broadening at the film/metal inter-

Fig. 10 Logarithmic plot of relative depth-resolution, $\Delta Z/Z$, and location of interface, Z , expressed in terms of thickness.

face obeyed approximately an error function except for the NiO/Ni system. The average sputtering rate of surface oxide film decreased in the order of NiO, Nb₂O₅, Fe₂O₃ and Cr₂O₃ films, whereas, the relative depth-resolution improved in the order of NiO/Ni, Fe₂O₃/Fe, Cr₂O₃/Cr and Nb₂O₅/Nb systems. The initial surface roughness and crystal orientation of the films in addition to the factors originated from sputter-etching itself was emphasized to be predominant factors influencing the depth-resolution.

REFERENCES

- (1) S. Hofmann: *Surface & Interf. Anal.*, **2** (1980), 148.
 - (2) C. Lea: *Met. Sci.*, **17** (1983), 357.
 - (3) R. N. Yasko and L. J. Fried: *Rev. Sci. Instr.*, **43** (1972), 335.
 - (4) N. S. McIntyre and D. G. Zetaruk: *J. Vac. Sci. Tech.*, **14** (1977), 181.
 - (5) R. G. Hart and G. W. Simmons: *J. Vac. Sci. Tech.*, **15** (1978), 714.
 - (6) D. F. Michell, G. I. Sproule and M. J. Graham: *J. Vac. Sci. Tech.*, **18** (1981), 690.
 - (7) M. Seo and N. Sato: *Oxid. Met.*, **19** (1983), 151.
 - (8) T. Ohtsuka: *Bull. Jpn. Inst. Met.*, **20** (1981), 614.
 - (9) R. Kelly and N. Q. Lam: *Radiat. Eff.*, **19** (1973), 39.
 - (10) S. Hofmann, J. Erlewein and A. Zalar: *Thin Solid Films*, **43** (1977), 275.
 - (11) S. Hofmann: *Appl. Phys.*, **9** (1976), 56.
 - (12) H. Oechsner: *Appl. Phys.*, **8** (1975), 185.
 - (13) H. Shimizu, M. Ono and K. Nakayama: *Surf. Sci.*, **36** (1973), 817.
 - (14) T. Ishitani and R. Shimizu: *Appl. Phys.*, **6** (1975), 241.
 - (15) S. Hofmann: *Appl. Phys.*, **13** (1977), 205.
-