

GD-OES/XPS Study of the Surface of Silicon Steel Sheets Annealed in Atmosphere with Various H_2O/H_2 Ratios

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GD-OES and XPS have been applied to analyze surface layers of silicon steels annealed in the atmosphere with various H_2O/H_2 ratios. GD-OES depth profiles show that internal oxidation in this steel occurs by increasing H_2O/H_2 ratio, and XPS spectra indicate that the surface amount of silicon and manganese in the surface decreases and the iron amount increases by increasing the H_2O/H_2 ratio in the annealing atmosphere.

1. Introduction

Oxide films formed on the surface of steel sheets play an important role in controlling surface properties, even if the thickness of these oxide films is of nanometer order of magnitude. The composition and morphology of these oxide films are affected not only by bulk composition but also annealing conditions such as atmosphere and temperature. For instance, different kinds of oxide films formed on the surface of silicon steel have been detected using infrared spectroscopy and so on, which provided some interesting information on the influence of the H_2O/H_2 ratio in annealing atmosphere on formation of oxide films. However, the influence of the H_2O/H_2 ratio on the chemical composition and state of these oxide films has not been fully understood [1]. The aim of the present work is to characterize oxide films formed on the surface of a silicon steel sheet annealed in different atmospheric conditions by means of glow discharge optical emission spectroscopy (GD-OES) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

A silicon steel sheet was produced through the process for grain-oriented silicon steel, with the main chemical composition of 3.25 mass%Si, 0.1 mass%Mn, 0.04 mass%Sn [2]. The microstructure consisted of secondary recrystallized grains, and the thickness of these sheets was 0.23 mm. Samples cut from the sheet were annealed in 25%N₂-75%H₂ with different H_2O/H_2 ratios at 1123 K for 30 s; these samples were annealed in the gas with the partial pressure ratio of water to hydrogen, H_2O/H_2 , of 0.013, 0.11 and 0.37, and are referred to as sample(a), (b) and (c), respectively. The gases had dew points of 280 K, 335 K and 344 K, respectively. These annealed samples were cut to about 10 mm square for GD-OES and XPS.

GD-OES and XPS were used for characterizing the chemical composition and state of oxide films formed on the surface of these sheets. A depth profiling method by GD-OES was reported previously [3,4]. In XPS, the incident X-ray used was monochromatized Al-K α , and the pass energy was 58.7 eV. The binding energies were determined in the accuracy within ± 0.2 eV. Ion sputtering by argon ions was done to

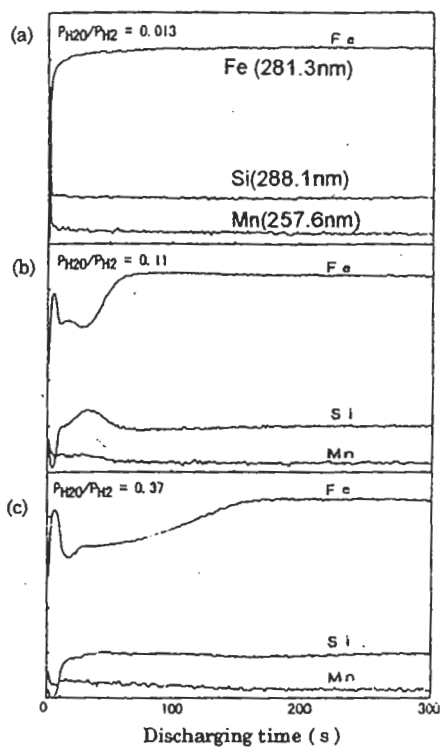


Fig.1 GD-OES depth profiles for samples annealed in the gas with the partial pressure ratio of water to hydrogen, H_2O/H_2 , of (a) 0.013, (b) 0.11 and (c) 0.37.

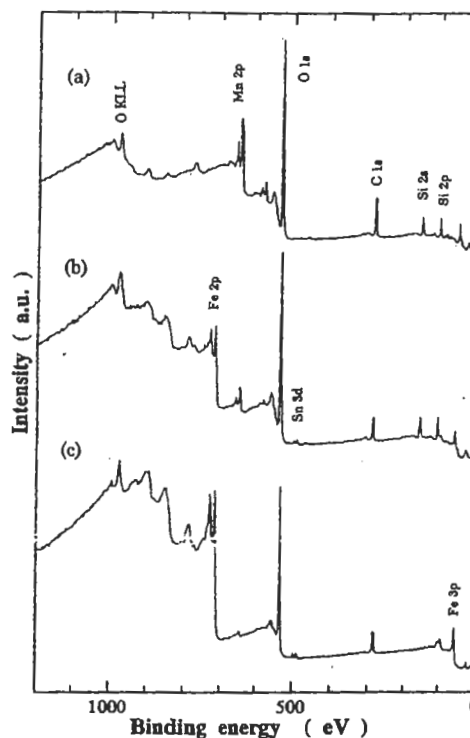


Fig.2 XPS wide spectra for samples annealed in the gas with the partial pressure ratio of water to hydrogen, H_2O/H_2 , of (a) 0.013, (b) 0.11 and (c) 0.37.

remove a contaminated layer adsorbed onto the sample surface.

3. Results and Discussion

Figures 1(a), (b) and (c) show GD-OES depth profiles from sample(a), (b) and (c) as prepared. These depth profiles indicate that compositional distribution is limited on a surface layer in the sample annealed in the atmosphere of low H_2O/H_2 ratio, while oxygen is penetrated into the sample annealed in the atmosphere of high H_2O/H_2 ratio. This suggests that internal oxidation occurs in this sample with increasing H_2O/H_2 ratio in the atmosphere. The thickness of the internal oxidation layer in sample(c) was evaluated to be about 3 micrometers from observation of the cross-section of the sheet.

In order to focus on elemental behaviors

on the surface thin layers, XPS measurements were conducted. Figs. 2(a), (b) and (c) show wide XPS spectra from sample(a), (b) and (c) as prepared, respectively. Systematic changes in the surface composition by annealing atmosphere are recognized, in spite of the identical bulk composition. The surface composition of these three samples was quantitatively evaluated with XPS peak intensities and the sensitive factors given in the software. XPS spectra of Si 2p, O 1s, Mn 2p, Sn 3d and Fe 2p were used for quantification of the surface composition, where the background of spectra was subtracted by the Shirley method. Before these measurements, the sample surface was sputtered for 10s, to remove contaminated layers, but not to remove the oxide layers so much. Table 1 summarizes the surface

Table 1 The surface composition (at%) of the sample (a), (b) and (c) annealed in the atmosphere with H₂O/H₂ ratios of 0.013, 0.11 and 0.37.

	Si	Mn	Sn	Fe	O
sample (a)	20.5	19.7	-	-	59.8
sample (b)	16.3	3.4	0.7	19.9	59.7
sample (c)	1.8	1.3	0.8	42.5	53.6

composition of main elements measured in these samples. They show that enrichment of silicon, manganese and tin on the surface strongly depends on annealing atmospheres. In particular, it is found that the amount of silicon and manganese in the surface layer decreases by increasing the partial pressure of water in the annealing atmosphere, whereas the iron amount in the surface layer increases by increasing the partial pressure of water.

In order to investigate the chemical state of the elements detected, details of XPS spectra were also compared. Figs. 3-6 show Si 2p, Mn 2p, Fe 2p and O 1s XPS spectra, which are clearly detected for these samples. (a), (b) and (c) in these figures denote the spectra for samples (a), (b) and (c), respectively. The ratio of signal to noise in the spectra for an element is reduced when the surface amount decreases. The main peaks of Si 2p, Mn 2p, Sn 3d and Fe 2p are located at about 130, 642, 486 and 711 eV, respectively, although Sn 3d spectra are not shown here. These results indicate that these metallic elements are oxidized on the surface. On the other hand, two components in the chemical state of O 1s XPS spectra, which correspond to peaks at about 530 and 532 eV, are observed, as shown in Fig. 6. The relative peak area of these components may be explained by changes in the chemical state of the counter elements. While the main peak of O 1s located at 532 eV, as shown in Fig. 6(a), originates from a Si-Mn oxide, the O 1s peak at 530 eV, as shown in Fig.6(c), is mainly due to Fe oxide layer. This oxidation behavior can be explained in terms of thermodynamic data of elements [1].

These XPS results on the surface thin

layer should be compared with GD-OES depth profiles as shown in Fig. 1, which indicate the occurrence of internal oxidation inside the sheets by different H₂O/H₂ ratios in the annealing atmosphere. In general, internal oxidation is accompanied by significant increase of the oxygen amount in silicon steels, which indicates the formation of fine silicon oxides in the steel [1]. This formation of silicon oxide can induce re-distribution or localization of iron and other elements in the internal oxidation layer and the surface. This may be the reason why the surface composition measured by XPS depends on the H₂O/H₂ ratio in the annealing atmosphere.

4. Concluding remarks

- (1) GD-OES depth profiles show that internal oxidation in this steel occurs by increasing H₂O/H₂ ratio in the atmosphere.
- (2) XPS spectra indicate that the surface amount of silicon and manganese in the surface decreases by increasing the H₂O/H₂ ratio in the annealing atmosphere, while the iron amount increases by increasing H₂O/H₂ ratio.
- (3) Silicon, manganese and iron of surface layers in these samples reveal oxide, and the chemical state of oxygen corresponds to the state of these elements.

5. References

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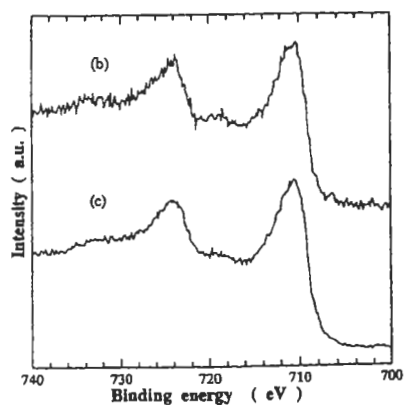


Fig.3 Fe 2p XPS spectra for sample (b) and (c).

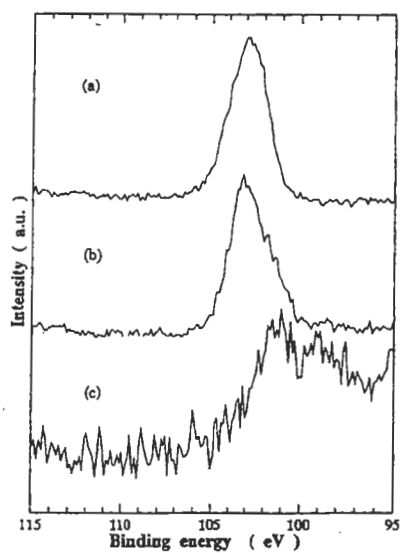


Fig.4 Si 2p XPS spectra for sample (a), (b) and (c).

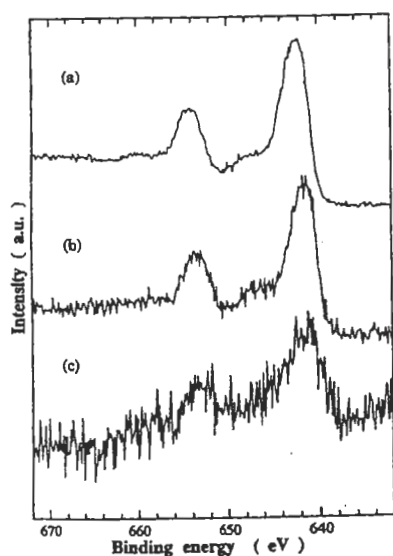


Fig.5 Mn 2p XPS spectra for sample (a), (b) and (c).

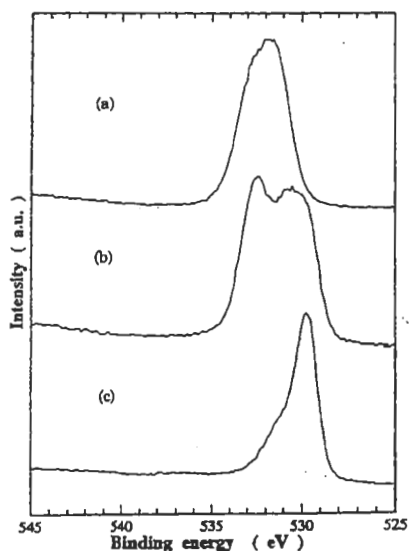


Fig.6 O 1s XPS spectra for sample (a), (b) and (c).