Time-of-fight Secondary Ion Mass Spectrometry of Oxide Layers Formed on the Surface of Silicon Steels

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(Received June 9 1997; accepted July 11 1997)

Time of flight secondary ion mass spectrometry (TOF-SIMS) with high mass resolution, which is a promising technique in surface analysis, has been employed for characterizing thin oxide layers formed on the surface of silicon steels. The specimens surface of cold rolled sheets was covered by an very thin oxide layer and a contaminated layer. TOF-SIMS could clearly resolve peaks of ions of iron, silicon molecule and contaminated species with the same nominal mass, providing reliable information of the thin layers. The present results show that iron is enriched to the outer side in the oxide layer formed at room temperature, and this corresponds to the results on characterization of thicker oxide layers thermally formed on the steel. Some characteristic features of secondary ion mass spectra such as contaminated organic compounds have also been recognized.

1. INTRODUCTION

Oxide layers formed on the surface of electrical silicon steels play an important role in processing of surface coating of silicon steels. Some investigations on thin oxide layers formed on the surface of silicon steels during decarburization, for instance, have been carried out using infrared reflection spectrometry, electron microprobe analysis and so on [1-3]. Although we can obtain the results of a few micron meters thickness of the oxide layers, further information on elemental compositions of very thin layers formed on the surface are required to understand the formation mechanism of the oxide layers. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) may be one way to such purpose, but there are several problems in characterizing those layers, because of low sensitivity of silicon peaks (Si 2p and 2s in XPS, Si KLL in AES) against iron peaks and peak interference between Fe MNN and Si LMM in AES. Since silicon is one of the most important elements in plain steels as well as silicon steels, such inconvenience is often encountered in surface characterization of steels.

Secondary ion mass spectrometry (SIMS) is also believed a powerful tool to analyze the solid surface. Figure 1 shows a depth profile of an Fe-4% Si sheet, which is the same as that shown later, obtained by a conventional SIMS technique with a quadrupole analyzer. In this experiment, the primary ions were oxygen ions with 5 keV, the sputtering rate was about 0.03 nm/s and the positive secondary ions were detected. The surface of the specimen was covered by a thin oxide layer due to air exposure. Iron, silicon, their hydroxide and oxygen ions were recorded with sputter time in this measurement, but their ion counts might include

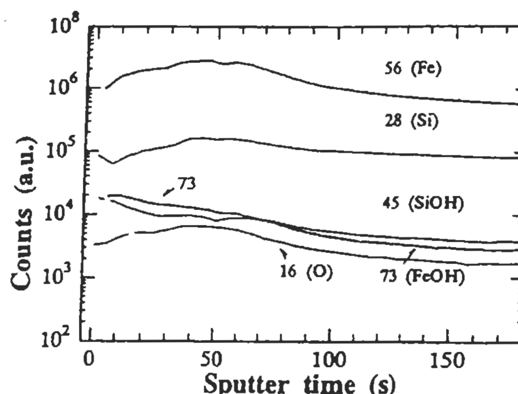

Fig.1 Depth profile of an Fe-4% Si sheet by conventional SIMS with a quadrupole analyzer.

Table 1 Possible interferences occurring in secondary ion mass spectra from silicon steel.

Mass number	Main ion(amu)	Interference ions (amu)
28	^{28}Si (27.977)	CO (27.995) N_2 (28.006) C_2H_4 (28.031)
54	^{54}Fe (55.940)	^{54}Cr (53.939) $^{27}Al_2$ (53.961) C_4H_6 (54.047)
56	^{56}Fe (55.939)	Si_2 (55.953) C_3H_4O (56.026) C_4H_8 (56.062)

different ions with the same nominal mass. In other words, the required information may be obscured, because some overlaps occur due to low mass resolution. Possible interferences occurring in secondary ion mass spectra from silicon steels are listed in Table 1.

On the other hand, time-of-flight secondary ion mass spectrometry (TOF-SIMS) with high mass resolution, which has recently been developed [4-6], is a promising method in analyzing a thin layer consisting of complicated constituents. This method appears to hold promise in reducing difficulty of the conventional quadrupole SIMS by detecting silicon, iron and other ions from the surface of silicon steels and obtaining reliable depth profiles. The aim of the present work is to provide preliminary results of thin oxide layers formed on the surface of silicon steels, and to discuss applicability of TOF-SIMS in surface characterization.

2. EXPERIMENTAL

Ingots of Fe- 2.0 and 4.1 mass % Si steels, referred to as Fe-2%Si and Fe-4%Si respectively, were produced by vacuum melting. They were hot rolled at about 1300 K to sheets of about 2 mm in thickness. Oxide scales formed on the surface were removed by pickling, and then the sheets were cold rolled to reduce their thickness of about 0.8 mm. Subsequently, they were washed with acetone to remove machine oil, and then their surface were analyzed by TOF-SIMS. Since the surface of silicon steels are easily oxidized in rolling at room temperature, an oxide layer should be considered in this work.

A TOF-SIMS apparatus (PHI TFS-2000) was used to analyze the surface in the present work. The primary ions were gallium ions accelerated to 15 keV, and the analyzed area was nine micron meter square. The mass resolution given by $m/\Delta m$ (m: mass, Δm: full width of half maximum of the peak) was about 8000 in mass about 56, as shown in Fig.2. It would be stressed that the spectrum of Fig.2 obtained for the top surface of Fe-2%Si clearly indicates Fe, Si_2 and C_4H_8 ions with sufficient resolution. Detection of contaminants and silicon by another type of TOF-SIMS has been reported for a contaminated silicon wafer [7]. Although a wide range of secondary ion mass spectra was recorded in the present work, our intention mainly focused on Fe, Si, FeOH, SiOH and O ions in the depth profiles. The sputtering rate obtaining for depth profile was about 0.05 nm/s

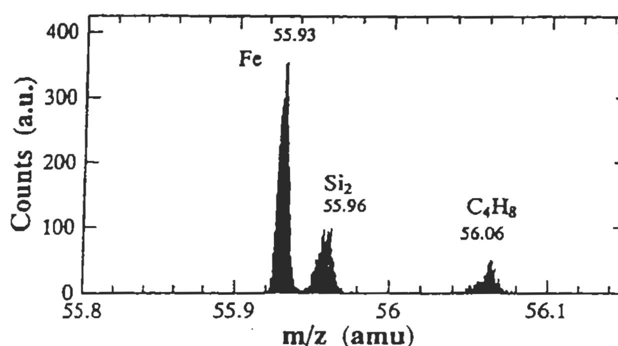

Fig.2 Secondary ion mass spectra from the top surface of Fe-2%Si.

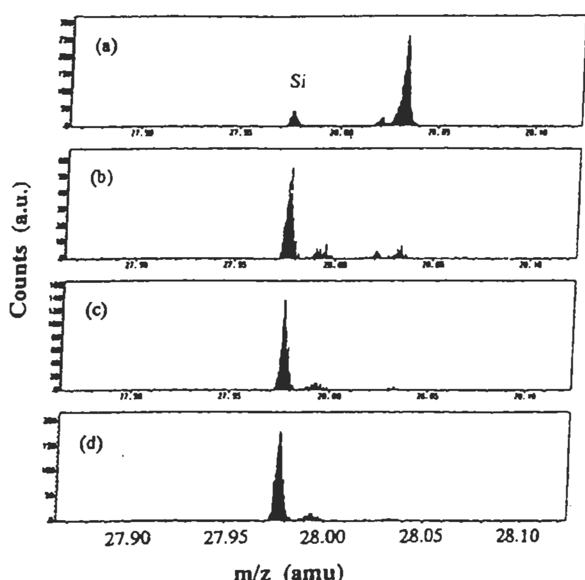

Fig.3 Secondary ion mass spectra close to 28 amu from the surface of Fe-4%Si in the sputtering time of (a) 0, (b) 5, (c) 10, and (d) 15 s.

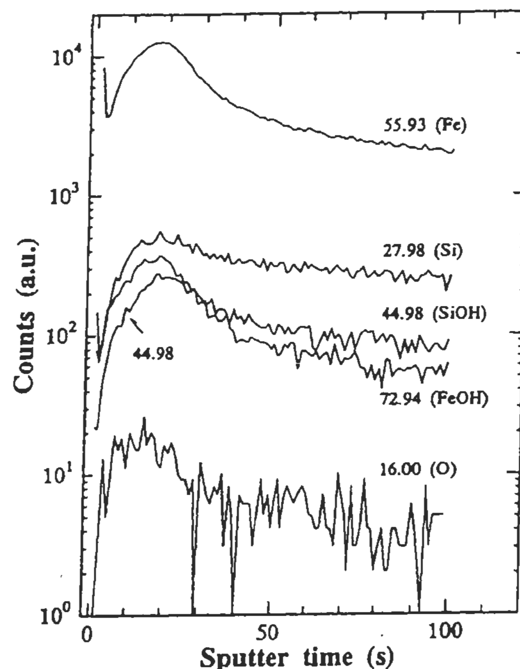

Fig.4 Depth profile of Fe, Si, FeOH and SiOH obtained from Fe-2%Si.

which was estimated using a SiO_2 film on a silicon wafer. Secondary ion mass spectra were measured with low doses of primary ions, when the sputtering was interrupted.

3. RESULTS AND DISCUSSION

1. Secondary ion mass spectra

Figure 3 shows secondary ion mass spectra near mass 28 from the surface of Fe-4%Si, where (a)-(d) correspond to the results with sputter time of 0, 5, 10 and 15 s, respectively. Ion peaks of Si (27.98 amu), and C_2H_4 (28.03 amu) are resolved owing to high mass resolution. The C_2H_4 peak is detected from the top surface, and it may originate from contaminated hydrocarbon adsorbed to the surface during air exposure [8]. The C_2H_4 peak is drastically decreased by sputtering, while the counts of silicon ions increase with sputtering.

In order to detect contaminated species other than the C_2H_4 peak, secondary ion mass spectra of high mass number were measured for the top surface. Many ion peaks such as mass 81, 91, 105, 115, 128 and 155, allocating to hydrocarbon CnHm (n,m: integers), were detected in the measurement. These signals may be attributed to fragment ions of contaminated organic compounds on the surface. Some fragment ions containing silicon have also been detected from the

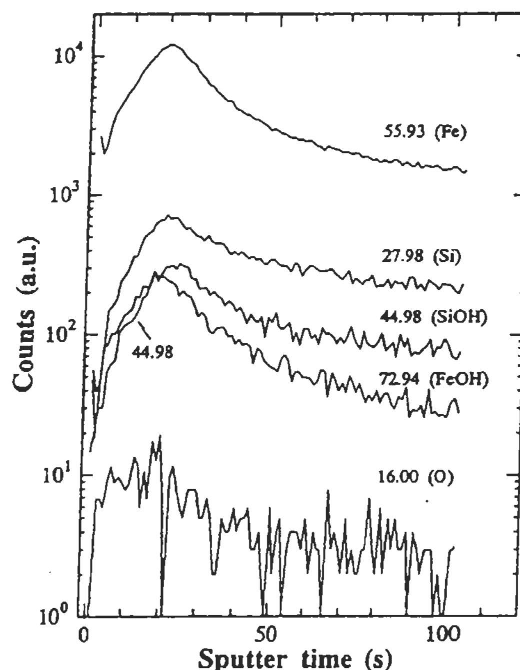

Fig.5 Depth profile of Fe, Si, FeOH and SiOH obtained from Fe-4%Si.

top surface, which may come from organic compounds such as residual rolling lubricant used in cold rolling. With this fact in mind, TOF-SIMS appears also to be applicable to analysis of organic

layers and coatings formed during processing, although the present work mainly focuses on contaminated hydrocarbon only.

2. Depth profiles

Figures 4 and 5 give the depth profiles from the surface of Fe-2%Si and Fe-4%Si, respectively. Following sputtering for 100s, the matrix of these specimens almost appears. It would be interesting to note that counts of secondary ions in the oxide layer are higher than those in the metal matrix. It may result from difference of the ionization process between the metal matrix and the oxide layer, similar to the iron base alloys [9-11]. Hydroxide (FeOH and SiOH) is likely to be formed by reaction with residual gases such as water and hydrogen, and their counts appear to be correlated with those of the metallic peaks (Fe and Si).

The ratio of Si peak to Fe peak in Fe-2%Si and Fe-4%Si as a function of sputter time is summarized in Fig.6. These results show that silicon is depleted on the outer side in the oxide layers; that is enrichment of iron in the oxide layers. Although the present oxide layers have formed at about room temperature, such characteristic distribution of the constituent element is found within the oxide layer. For instance, it has been reported that iron is enriched to the outer side of the oxide layers on iron base alloys during thermal oxidation [12]. The non-linear increase of Si intensity by bulk silicon concentration may be attributed to difference of feature of those oxide layers. The present results indicate that such behavior in oxidation at high temperature takes place even at room temperature.

The potential capability of TOF-SIMS for analyzing different ions with a similar mass from very thin layers, has been well recognized by the present results of silicon steels, although some further developments are still required before it can be accepted as a very reliable quantitative technique. Since this method can be used for obtaining images of secondary ions from small area, it would also reduce difficulties in surface characterization of solids materials.

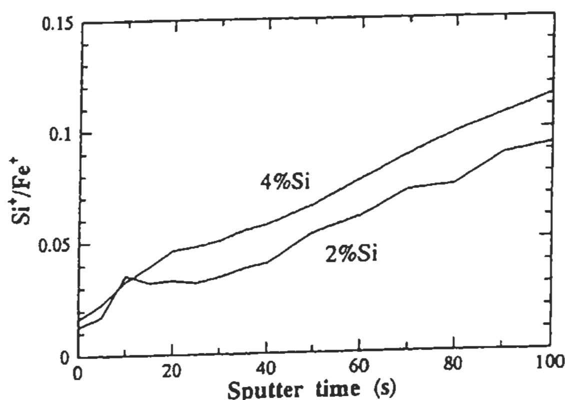

Fig.6 The ratio Si^+ counts to Fe^+ counts as a function of sputter time.

4. CONCLUDING REMARKS

TOF-SIMS has been used for characterizing thin oxide layers formed on the surface of silicon steels.

(1) Peaks of secondary ion mass with a similar mass number were successfully resolved to in TOF-SIMS. Thereby, elemental information can be obtained in depth profiles without any interference.

(2) Every secondary ion counts of the oxide layers werehigher than that in the metal matrix in the depth profiling process, which may be attributed to the matrix effect.

(3) Iron was found to be enriched to the surface side in the oxide layer formed at room temperature. This is consistent with the previous result on the oxide layers thermally formed in silicon steels.

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査読者との議論

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笹川　薫　（（株）コベルコ科研）

1. この系において、AES,XPS では、感度・定量性が低いということですが、TOF-SIMS における定量性の問題点はどうお考えでしょうか？（in Introduction）（林）

答：　ここでは、厳密な定量的議論は、あまり期待しておりませんでした。むしろ、Ｓｉがどのように検出されるを調べるのが目的でした。この系で、他の方法で得にくいＳｉの確からしい信号を得ただけで、少し手応えを感じております。

2. TOF-SIMS において、0.5nm/sec というスパッタ速度は非常に大きい値のように感じられますが、これは正しいのでしょうか？その時のパルス幅、繰り返しはどのくらいですか？(in Experimentals)（林）

答：　ご指摘の通り、このスパッタ速度は間違いです。だいたい０．０５ｎｍ／ｓ（深さ方向分析時）程度です。失礼いたしました。

3. Fig.6 において、2%Si と 4%Si の二次イオン強度が 1:2 にならないのは、どうしてですか？高分解能測定であるため、マスインターフェアレンスでは説明できませんね。（林）

答：　多分、試料上に形成する酸化皮膜のＳｉ濃度による違いかと思われます。Ｓｉ濃度は表面酸化層の形成に対し大きく影響します。本当ならば、十分基板まで分析して比べたかったのですが、都合によりできませんでした。

4. TOF-SIMS におけるマトリックス効果はどのように考えられますか？即ち、この条件においては Ga の一次イオンが大量に注入されています。また、パルスイオンビームにおいては、酸素・水分の再吸着が無視できません。それとも、このスパッタ速度なら再吸着は無視できるのですか？その場合、スパッタ面積に対して、分析面積はどのような関係にありますか？酸素が再吸着するのなら、酸化膜とのマトリックス効果は低減される方向になるとは思います。例えば、パルス幅依存性やパルス繰り返し依存性などは無いのでしょうか？（林）

答：　ご指摘のように、この種の実験ではマトリックス効果が大きいものと考えられます。固体へのイオン侵入、一次イオンとそれぞれの層との相互作用、二次イオン・原子の放出、再吸着等を、測定時の表面構成層に対してそれぞれの過程を考え、結果として得られる二次イオン信号が何を意味しているのかを明らかにすることによって、マトリックス効果に対する知見が得られてくるものと思われます。しかし、それらの因子を明かにするには、精密な実験が必要と考えられます。また、ご指摘のように、試料状態のみならず、分析面積などの測定条件もその過程に影響しますので、定量的（？）に議論する際には、それらの条件も変化させることによって、マトリックス効果の内容が明らかになると思います。

5. Conclusion (3)は TOF-SIMS で、はじめて明らかにされたのですか？（林）

答：　この系での室温付近の酸化に対しては、はじめてでしょう。しかし、経験的には表面近傍で、反応に伴い構成原子の再配列が起こるというのは感じておられるかと思います。

6. TOF-SIMS を使う理由として、質量電荷比が同じイオンの重なりによる妨害を挙げ、Convensional SIMS として質量分解能の低いＱ pole SIMS と比較していますが、質量分解能の高いセクタータイプの SIMS と比較したほ

うが自然なように思えるのですがいかがでしょうか。例えば高質量分解能モードではセクターよりTOFのほうが感度が良いとか・・・。（笹川）

答：　おっしゃる通りです。ここでは、セクター型ＳＩＭＳで実験していないため、一般的な四重極ＳＩＭＳの結果との比較だけを行っております。極表層の分析に対し、どのタイプが有効かは、試料の素性にもよるかと思いますが、ここではとりあえず、Ｑ型とＴＯＦ型の二つで調べて見ました。

7.　室温で生じた酸化膜の評価ということですが、通常の冷延プロセスではかなり温度上昇があると思われるのですがいかがでしょうか。（笹川）

答：　連続冷間圧延ですと温度が上昇しますが、ラボ的に圧延しておりますので、パス間の合間があるため、それほど顕著でないと思います。もちろん、そこで形成した酸化層が、実験結果に影響しているものと考えられます。

8.　Fig.1の測定時のスパッタ速度はいくらでしょうか。（笹川）

答：　有効速度０．０３ｎｍ／ｓ程度です。

9.　Fig.1とFig.4,5の縦軸のスケールを合わせたほうが比較しやすいと思います。（笹川）

答：　ご指摘の通りですが、データ出力が異なるため、あわせるのが困難です。

10.　Fig.1のQ-SIMSによるデプスプロファイルでは４５と７３の質量数のイオン強度は表面ほど高いのに対して、Fig.4, Fig.5のTOF-SIMSによるデプスプロファイルではスパッタ時間約２０秒を最大に、表面のほうが低くなっていますが、この原因として何が考えられるのでしょうか。（笹川）

答：　これら試料の条件は同一と見ておりますが、測定のタイミング等で表面状態が変化している可能性もあり、何ともいえません。

11.　Fig.4,5で、酸化層中の二次イオン強度が母材金属中のそれよりも高いのは酸素による増感でしょうが、表面から１０ないし２０秒までの間で二次イオン強度が増大している理由は、残留圧延油やコンタミ炭化水素のためでしょうか。（笹川）

答：　多分、ご指摘の通り、表面層の何らかの影響で二次イオン強度が微妙に変化しているものかと思われます。

12.　TOF-SIMSによる最表面の分析では、分析対象試料表面の履歴が非常に重要だと考えられます。今回の試料の場合、最表面で圧延油？やコンタミの炭化水素が検出されたとのことですが、アセトン洗浄は何のために行ったのでしょうか。蒸留水、エタノール、イソプロピルアルコールなどとの使い分けについて何かコメントしていただければ、ありがたいのですが。

答：　初期状態を大体そろえるのを目的に、一般的に使われるアセトンを用いました。それでも汚染はとれていませんが、厚めについた油成分はとれたかと思います。洗浄液には何が適当かは、まだわかりません。今後の課題かと思われます。