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ORIGINAL PAPERS**A New Analytical Technique for Insulating Materials
by Means of an Ion Microanalyzer**

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The ion microanalyzer (IMA) analyzes the secondary ions sputtered from the target which has been bombarded by the primary ions. In the analysis of insulating materials by an IMA, the electrostatic charge accumulated on the specimen surface interrupts the detection of the secondary ions.

In this paper we report that, with the use of a low energy electron gun, the interruption mentioned above is prevented effectively and it is able to analyze steadily the secondary ions sputtered from insulating materials.

1. Introduction

It is well known that the secondary electron yield is greater than one, when an insulator was bombarded by ions having an energy of a few to tens of keV. With such an ion bombardment, the surface of the specimen becomes positively charged. When negative ions are used as primary ions, the surface potential increases with time until a critical value is reached, at which the emitted electrons are drawn back to the specimen by the surface potential and this causes "charge compensation". Consequently, the surface potential attains to a constant value in due time.¹⁾

If positive ions are used as primary

ions, however, the surface potential is not compensated but continuously increased, so that discharge takes place between the specimen holder and the specimen. Accordingly, the surface potential always fluctuates. This surface potential fluctuation causes the initial velocity of secondary ions to change and makes ion microanalyzer analysis very difficult.

In order to solve the problem of charge accumulation, we have developed a new analytical technique—the electron spray method. Its principle is to compensate the surface charge by spraying low energy electrons over the surface which has been bombarded by the primary ion beam.

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2. Mechanism of Charge Compensation

Fig. 1 is a schematic illustration of the various currents which can occur at the target and its surroundings when a primary ion current bombards the target. The insulator is covered with a conductor held at earth potential and bombarded by both primary ions and low energy electrons. In this figure, I_1^i represents the incident primary ion current, I_1^e the incident primary electron current, η^i and η^e the secondary electron yields due to ion and electron bombardments, respectively.

Giving an appropriate energy to the incident primary electrons, η^e can be made considerably greater than η^i . The specimen surface is positively charged as secondary electrons are emitted from it. With the specimen surface positively charged, the emitted secondary electrons cannot flow into the conductor held at earth potential and are drawn back to the specimen, causing charge compensation. The condition for charge compensation taking place on the specimen surface can be given by the following equation.

Fig.1. The mechanism of charge compensation.

$$I_1^i - I_1^e + \eta^i I_1^i + \eta^e I_1^e \leq K(\eta^i I_1^i + \eta^e I_1^e) \quad (1)$$

The left side of Eq. (1) represents the charging current which flows into the specimen, and the right side shows the charging current drawn back to the specimen by the secondary electrons. Eq. (1) can be rewritten as follows:

$$\frac{I_1^e}{I_1^i} \geq \frac{1 + (1-K)\eta^i}{1 - (1-K)\eta^e} \quad (2)$$

In these equations, K , η^i , η^e have constant values. Thus, the condition for charge compensation can be fulfilled by giving an appropriate value of I_1^e for the given I_1^i .

3. Experiments

Fig. 2 shows the arrangement for preliminary experiments with the electron spray gun to use for charge compensation. In order to unify the electron beam density on the specimen surface, Pierce type was adopted as the electron spray gun.²⁾

The purpose of this experiment is to investigate the focusing condition for the electron beam and character of the electron spray gun. A positive high voltage is applied to the fluorescent screen and hemispherical shielding electrode made by wire gauze covering it. The cathode is kept at earth potential. I_1 and I_2 are the ammeters for the measurement of emission and heating currents, respectively. The distance between the anode and cathode is adjusted so as to obtain a beam of about 10 mm in diameter on the fluorescent screen. Beam diameter of 10 mm was chosen in order to spray electrons cover the entire specimen surface.

The characteristics of the electron spray gun is shown in Fig.3. The filament heating current is shown on the abscissa

Fig. 2. The arrangement for preliminary experiments.

and the emission current on the ordinate. This figure demonstrates that the emission current increases sharply with increase of the heating current and then attains to a saturation level. The saturation level indicates a space charge limited current. Fig. 3 also shows that the emission current increases with increase of the accelerating voltage.

The electron spray gun used for preliminary experiments was mounted on the ion microanalyzer (Hitachi Model IMA-2). The features of the newly developed charge compensation system may be summarized as follows:

- (1) The secondary ion accelerating voltage is employed for the accelerating voltage of electron spraying.
- (2) The electron gun is of Pierce type consisting of the shield electrode located above the specimen and cathode, assuring a highly stable

Fig. 3. Characteristics of the spray gun.

electron beam over the specimen.

In Fig.4, the schematic diagram of the specimen chamber and in Fig.5, the external view of IMA-2 are shown. The ion microanalyzer mainly consists of the primary ion illuminating system, the scanning ion microscope and the double focusing mass spectrometer. Overall design of IMA-2 is determined by the horizontal sample stage for the ease of sample handling and for the arrangement of simultaneous ion and electron detection system. The primary ion beam bombards the specimen perpendicularly, and the taking-off angles of these detectors are 45°. Primary ion probing spot itself serves as the source for the secondary ion optics. This helps high sensitive ion detection. The secondary ion detection system is rather a mass spectrograph (Mattauch type) than a mass spectrometer, because the detecting information from the specimen

Fig. 4. Specimen chamber of a Hitachi IMA-2.

Fig. 5. Hitachi model IMA-2 ion microanalyzer.

depends upon time and needs to be recorded simultaneously with the change of the sputtered specimen surface.

In the following experiments of insula-

tor analysis, the BK-7 glass was used. The composition of BK-7 is shown in Table 1.³⁾

The relationship between the sprayed

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Table 1. The composition of the BK-7 glass.

Component	Concentration (%)
SiO ₂	68.9
B ₂ O ₃	10.1
Na ₂ O	8.8
K ₂ O	8.4
BaO	2.8
As ₂ O ₃	1.0
Total	100.0

electron current and the stability of the secondary ion current is shown in Fig.6. The main component of BK-7 is SiO₂. The mass spectrometer is therefore adjusted for detecting the ²⁸Si⁺ ion and the ²⁸Si⁺ ion current was measured with variation of the sprayed electron current. In the state (1), the specimen had not been bombarded with electrons so that the secondary ion was scarcely detectable owing to

surface charging. In the states (3) and (4), the surface was bombarded with an electron beam of 5×10^{-5} A/cm² density. The secondary ion yield showed a sharp increase followed by a decrease.

It is assumed that the surface charge was compensated initially, but owing to the insufficient primary electron current, the charge accumulated with time caused the secondary ion yield to decrease. In other words, this can be regarded as a transient state. The state (5) represents a stable state in which the surface charge is compensated with electrons. This means that this is the state where the expressions (1) and (2) are being satisfied.

The mass spectrum of BK-7 is shown in Fig.7. Background test for the electron spray gun is represented in the state (i). In the state (ii), the analysis by the ion beam only (electrons were not sprayed) is

Fig. 6. Relationship between the sprayed electron current and stability of the secondary ion current for BK-7.

represented. The state (iii) represents the analysis by the electron spray method. Primary ion beam density was about 6×10^{-5} A/cm² and the electron beam density was about 5×10^{-5} A/cm². In order to compare the spectrum of the insulating material with that of the conductive material, a mass spectrum of the standard steel alloy is shown in Fig.8.

From these experimental results, it was found that:

- (1) The background due to electron spraying is negligible, if any.
- (2) The main components of BK-7 (Si, B, Na, K, As, O) were all detected. C, Al and Fe were also detected.
- (3) When electrons were not sprayed, the elements listed above were not detected with the exception of K

and Si, small quantities of these two elements being detected.

- (4) Comparing the spectrum in Fig.7 with that for steel in Fig.8, the resolution was not affected by the sprayed electrons.

4. Applications

Fig.9 shows a mass spectrum of mica obtained by the electron spray method.

Fig.10 shows a mass spectrum of alumina powder used as a column packing material in gas chromatography. The specimen was prepared in a pellet form by compression molding. Although mica and alumina have a high dielectric constant, the spectra obtained by the electron spray method were quite stable.

In Fig.11, an example of another application of electron spraying is shown. Sample

Fig. 7. Mass spectrum of BK-7.

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Fig. 8. Mass spectrum of the standard steel alloy.

Fig. 9. Mass spectrum of mica.

Fig. 10. Mass spectrum of alumina.

Fig. 11. Mass spectra of stainless steel 32.

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analyzed was stainless steel 32. The mass spectra of Cr and Fe, the main components of stainless steel, were measured with the electron bombardment increased gradually. It has been shown that:

(1) The sensitivity was increased by about 10 % in the saturated state.

(2) The resolution was not degraded at all by the electron bombardment.

The increase in the sensitivity is probably due to the ionization of neutral atoms.

5. Conclusion

The electron spray method is powerful means for the analysis of insulating materials. As a future problem, we are interested in heating effects and improvement

of the ion yielding efficiency in the electron spray gun.

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