Development of an Electron-Beam-Excited Plasma SNMS SNART (2)*

James W. BRADLEY** and Shigeki KATO**

Institute of Physical and Chemical Research, Wako-shi, 351-01, Japan

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We report on the further development of a sputtered neutral mass spectrometer known as SNART (sputtered neutral analysis-RIKEN type) which has been developed to provide a means for quantitative analysis of bulk or surface compositions of both insulating and conducting materials. In this system both high sputter-etch rates (few nm/s) at low bombarding energy (about 100 eV) and high postionization probabilities (20%) are achievable using a dense (10^{13} cm^{-3}) magnetically confined argon plasma discharge driven by a low-energy electron beam (100 eV) with typical beam current of 1–2 A.

SNART has potential for high detection sensitivity and capability for both insulator analysis without a charge neutralizer and high depth resolution with quick analysis.

The relative sensitivity factors for trace elements in both conducting and insulating samples at standard operating conditions have been determined and the machine performance as a function of the operating conditions investigated.

1. INTRODUCTION

It has been shown previously that SNART provides both the means for material depth profiling of multilayered structures (depth resolution of about 1 nm at a sputtering rate of 0.9 nm/s) and the potential for quantitative analysis of atomic composition of the surface and bulk^{1),2)}.

In addition SNART has many advantages over conventional analysis techniques involving sputtering. For example in SIMS, atomic mixing and ion-induced roughness due to large impact energies prevent high depth resolution ($> 3 \text{ nm}$ at a 0.014 nm/s sputtering rate). SNART also allows separation of

sputtering and ionization processes in contrast to SIMS. The merits of both techniques have been discussed by Kato *et al.* in¹⁾.

In SNART, material sputtering and postionization of sputtered neutrals are achieved using an electron-beam-excited, E.B.E. plasma. This high-density discharge is maintained against losses by the impact ionization of neutral argon atoms by beam-accelerated magnetized electrons originating from a conventional glow discharge source. The distribution of electron energies in the E.B.E. plasma shows a distinct high-energy tail superimposed on a collisionally relaxed thermal background of typically several eV temperature³⁾. It is a characteristic of this source that deep sheath potentials (drop between sample V_f and plasma V_p) are generated to sample surfaces perpendicular to the beam flow, resulting in sample sputtering by plasma ions. Also, the probability of postionization of sputtered atoms is high. Both these effects are directly due to the presence of the electron beam component. Typically, at low working pressures (long collision lengths), we find that the magnitude of the sheath potential V_{sh} is close to that of the beam acceleration potential and is considerably larger than those generated on the principle of a cool, purely Maxwellian electron energy distribution. Since the resulting E.B.E. plasma is quasi-neutral, SNART has the capability to analyze insulating samples without a neutralizer for charge compensation at the target. Both bombarding ion energy and flux are controlled by the ion sheath established between the plasma and the surface. The nature of the sheath itself is critically dependent on the plasma conditions. In this system we can independently control the sputtering energy and bombarding ion flux by simply varying the plasma discharge conditions. Despite the low sputtering

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** 理化学研究所 (〒351-01 和光市広沢 2-1)

Fig. 1 Schematic layout of SNART-2.

energy (100 eV), high ion current densities of several tens of mA/cm² at the target position can be achieved, giving sputtering rates of a few tens of nm/s.

In the present work we shall report on the results of analysis carried out with standard samples. Relative sensitivity factors for trace elements in both insulating and conducting samples have been determined at standard operating conditions, and the machine response to changing discharge parameters is also investigated.

2. EXPERIMENTAL

The principle of use and characteristics of the E.B.E. plasma as an ion source have been described previously⁴. However, after recent developments, the glow discharge in region 1 and the working chamber in region 3 have been modified for SNART-2, which is shown in Fig. 1. Details of recent modifications for SNART-2 are described elsewhere⁵.

In brief, electrons produced in the glow discharge plasma are accelerated to energy V_a (typically 100 eV) in region 2 and subsequently flow into region 3 in the form of an electron beam guided by an axial magnetic field (typically, several hundred Gauss). The mechanism for the electron acceleration in a region close to electrode A1 is not well understood and is currently being investigated by several workers. In region 3 where Ar gas is introduced, a dense plasma is formed as a result of

impact ionization of neutral atoms by the electron beam (electrons in the tail of the collisionally relaxed thermal distribution will also contribute to ionization). Calculations based on Langmuir probe measurements have shown a postionization probability of over 20%¹. Charged particle diffusion losses to the walls are reduced in this region by the magnetic field, which counteracts the plasma expansion and results in the formation of a dense narrow plasma column. Some of the ions created in region 3 are accelerated back into region 2, thus reducing the electron space charge in the accelerating region. Hence, the electron beam is steadily maintained without a current limit.

The design of SNART-2 allows for analysis of both insulating and conducting samples⁵. In the latter case, the sample is placed with its surface normal to the beam direction and usually positioned about 10 mm from the beam axis. The sample surface potential (up to 600 v) is regulated independently of the plasma using a voltage power supply. For insulator analysis the sample is oriented at an angle of 45° to the beam direction and situated at the beam centre. In both cases the sample and housing are cooled by liquid nitrogen. An electrically floating ion extractor plate which forms the first electrode in the extraction lens system is located directly across the beam axis. Positionized sputtered particles and argon ions are accelerated through the extractor sheath normal to the beam and are focussed through a set of lenses to a quadrupole mass spectrometer situated 75 cm from the beam axis. The extracted beam flux (up to 500 uA) and ion energy (typically 20 eV) are a function of the edge plasma parameters. Retuning of the ion optics is necessary after the discharge parameters have been changed due to variations in the optic focal lengths with initial conditions. Recent improvements in the ion optics design (lens positioning and dimensions) have increased the transmission to the quadrupole orifice from 10⁻⁴% to 0.03%. The target holder is equipped with a shield apparatus which floats electrically in the plasma. With the present operating conditions it is unavoidable that the holder is sputtered during analysis of the insulators. The opening diameter can be chosen so as to restrict the sputtered area A_{sp} . Typically, for conductors we have $A_{sp}=25$ mm² and for insulators 125 mm². In normal operation the potential of electrode A1 is set at +30 v relative to machine ground. Since the plasma is tied electrically to A1 and ions at the Faraday cup are collected at ground potential, the overall ion pass energy is low. This is necessary since, with this type

of mass spectrometer, the mass resolution deteriorates with increasing ion pass energy (increasing detected current).

The base pressure of SNART-2, which is pumped by a turbomolecular pump, is on the order of 10^{-5} Pa (the mass spectrometer is pumped differentially by a diffusion pump). SNART is operated in a working regime which depends on the mode of the analysis. Typically for insulators we have the following set of conditions: Ar glow discharge current of 2–3 A, electron energy of 30–100 eV in region 2, electron beam current of 0.5–1.5 A, Ar gas pressure in the working chamber of 0.2 Pa, ion bombarding energy between 50–150 eV and current density at the target of up to 4 mA/cm². For conducting samples we use higher glow discharge currents (about 5 A), and beam currents (about 3 A) with an electron energy of 30–40 eV. In this mode sputtering is achieved by external biasing and not through self-biasing.

To determine the machine performance, standard conducting and insulating samples have been analyzed. In the case of metals, Fe-, Ni-, Al- and Cu-based alloys were used, while insulating samples consisted of Si-based materials such as standard glass, SiO₂, SiC and some ceramics. Typically, the samples were 30-mm-diameter discs of 2–3 mm thickness. The liquid nitrogen cooling system was found to reduce the sample back-side temperature to between -100 and $+100^{\circ}\text{C}$ depending on the discharge conditions, the thermal conductivity of the samples and the dimensions. Occasionally, in the case of insulator analysis, thermal gradients leading to cracking of the sample posed a large problem. As a result, it was necessary to limit the power loading of the sample surface to 0.5 Watts/cm². We should note that at low sputtering energies the removal rate is almost proportional to the surface power loading; thus, some compromise is necessary.

To aid in the understanding of the machine response, beam property characteristics at different discharge conditions were investigated in a separate experiment by replacing the insulating sample with a small 1.5-mm-diameter plane Langmuir probe, insulated from the supporting sample holder.

3. RESULTS AND DISCUSSION

The ion current of a species detected at the mass spectrometer will be a function of its sputtering rate, the efficiency of postionization and transport to the extraction orifice and transmission through the ion optics system. The element detection

Fig. 2 The sheath potential (broken line) and ion saturation current (solid line) measured by a plane probe at the sample position as a function of the electron acceleration potential at different beam currents in SNART. $\cdots \circ \cdots$ $I=0.5$ A, $\cdots \square \cdots$ $I=0.75$ A, $\cdots \diamond \cdots$ $I=1.0$ A, $\cdots \triangle \cdots$ $I=1.5$ A.

efficiency factor gives us a measure of the general machine response to changing working conditions and is defined as the ratio of the ion count-rate measured at the mass spectrometer to the number of atoms sputtered per second at the target. **Fig. 2** shows the sheath potential and ion saturation currents to the plane probe as a function of electron beam energy at different beam currents. The beam current was varied by controlling the glow discharge current at constant pressure (gas flow rate). Characteristically, at low pressures the sheath potential $V_s (= V_f - V_p)$ decreases with increasing electron energy. For $I=1.5$ A, V_s falls sharply to -160 v at $V_a=100$ v. In contrast, the ion saturation current is seen to be almost independent of the beam energy for constant I . The probe was replaced with a SiC sample and sputtered for several minutes at the same values of discharge parameters. **Fig. 3(a)** shows the detected Si ion current measured at the Faraday cup. With the use of the probe measurements and sputtering yield data⁶, the Si neutral sputtering rate was determined. Typically, with V_a at 75 v and $I=1.0$ A, the sputtered flux is estimated at 1.2×10^{16} atoms/s from a 0.78 cm² exposed area, which corresponds to an etching rate of 0.15 $\mu\text{m}/\text{min}$. **Fig. 3(b)** shows that the calculated detection efficiency for Si in SiC is generally constant (approx 4×10^{-8}) with changing V_a and I , except for a decrease with high energy and a spuriously high value at $V_a=30$ v which may be due to the uncertainty in the theoretical sputtering yield at low energy. Generally there is low variability in the machine response (less than one order of magnitude) over a wide range of conditions.

Fig. 3 (a) The Si ion current detected at the mass spectrometer and (b) detection efficiency as a function of the electron accelerating potential for different beam currents I , from the sputtering of SiC in SNART. —●— $I=0.5$ A, —■— $I=0.75$ A, —◆— $I=1.0$ A, —×— $I=1.5$ A.

To assess the capability of SNART as a tool for quantitative analysis of insulators, it is necessary to determine the reproducibility from run to run in element sensitivity over the entire mass range and measure the variability in relative sensitivity of trace elements for different matrix types. The analysis of standard insulating and conducting samples (the trace element concentrations vary by three orders of magnitude for the sample types) allows us to evaluate the machine response of SNART.

We define a measurable relative sensitivity factor, r.s.f. (in reference to a particular element) which encompasses all machine sensitivities as follows:

$$\text{r.s.f.} = I_{\text{td}} C_{\text{rk}} / I_{\text{rd}} C_{\text{tk}}$$

where I_{td} is the detected trace element ion current, C_{rk} is the known concentration of the reference element (atomic %), I_{rd} is the detected ion current of the reference element and C_{tk} is the known trace element concentration (atomic %). Typically, the matrix element is chosen as the reference or, for cross-sample comparison, Fe for conductors and Si for insulators are chosen. **Fig. 4** shows a typical

Fig. 4 Mass spectra of standard glass g1412 scanned at 0.64 amu/s in SNART.

Fig. 5 The relative sensitivity factors (relative to Si) for low-mass trace elements plotted against increasing mass (nonlinear scale) obtained from the analysis of standard glass samples; ● g1411, □ g1412. Ar sputtering energy is 100 eV, beam current 0.8 A, and V_a is 88v.

($m/e < 66$) mass spectrum from the analysis of glass g1412. Some elements have been identified. A matrix (Si ion) current measured at 5×10^{-11} A and a detectable signal above the mean background of 1.6×10^{-17} A (at typical electron multiplier gain) gives a trace element detection limit of 0.4 ppm. In the case of conducting samples where higher beam currents and sputtering voltages give a sputtering rate higher by one order of magnitude, the detection limit is improved to 40 ppb. **Fig. 5** and **Fig. 6** show the r.s.f.'s (averaged over 3 to 6 runs) determined at constant conditions for both insulating and conducting standard samples.

There was excellent reproducibility from run to run (<5% spread for up to 6 repetitions), but results for both metals and glass show some variability from sample to sample. High-mass, low-melting-point elements such as Pb and Sn and volatile low-mass elements such as P show a large matrix dependency with generally very high r.s.f. (very small relative detection). On the other hand,

Fig. 6 The relative sensitivity factors (relative to Fe) for trace elements plotted against increasing mass (nonlinear scale) obtained from the analysis of standard metallic samples. Ar sputtering energy is 500 eV, beam current 3.0 A, and V_a is 40v.

mid-range elements such as Ni, Co and Mo, show little matrix dependency and have r.s.f. values within one order of magnitude of unity. Since the cross section for the single ionization of atomic species is fairly constant with increasing atomic mass^{7),8),9)}, the variability in detection may be due to the system being sensitive to the spatial distribution of sputtered neutrals or variable sample heating leading to thermally enhanced sputtering or evaporation of certain elements.

In SNART, resputtering of sputter-deposited material at the vessel walls (predominantly Cu from the sample holder) and sputtering of the lens stack system was not observed (detection < 1 ppm). SNART shows no memory effects.

4. CONCLUSIONS

Effective sputtering of insulating materials (etching rates of several nm/s) and efficient positionization of sputtered neutrals (20% positionization probability) are achievable in SNART. Improvement in the ion optic system has allowed the acquisition of insulating material mass spectra with a detection sensitivity of 5 ppm at very low sputtering energy (< 150 eV).

Measurements of machine performance have shown that the detection efficiency (detected ion current/neutral sputtering flux) for the Si matrix (Si in SiC) is fairly constant (< one order of magnitude) over a large range of discharge parameters. Run to run reproducibility in the

observed concentrations is good (< 5%), and over most of the elemental mass range for nonvolatiles, the relative element sensitivity factors (insulators and conductors) vary by less than one order of magnitude from matrix to matrix. This gives SNART the potential for semiquantitative analysis of nonstandard samples, with clear advantages over SIMS, where secondary ion yields vary over six orders of magnitude even in standard operating conditions. The large variability in r.s.f.'s with matrix element observed for low-mass volatile and also high-mass low-melting-point elements poses a problem. Spuriously large or small r.s.f.'s for non-volatile elements such as Mn in Al alloy are difficult to understand, and should be investigated further. Improved cooling of the sample surface may be one solution.

The trace element detection limit should be reduced further. This may be achieved by: a) improving the transmission of the ion optics, b) orienting the sample so its surface is perpendicular to the beam, or c) redesigning the detection system so that the angle between the beam axis, sample surface and extraction plate corresponds to the peak in spatial distribution of sputtered particles (70–80°). Implementing these changes may increase the detection limit by two orders of magnitude.

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