Plasma studies on the Leybold–Heraeus INA3 secondary neutral mass spectrometry system

A. Wucher

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 3 August 1987; accepted 13 December 1987)

Electron gas secondary neutral mass spectrometry (SNMS) has been introduced recently by Leybold–Heraeus (LH) as a commercially available method for quantitative surface and bulk analysis of solids. Being the central part of electron gas SNMS, the employed special low-pressure rf discharge has to be characterized carefully in terms of electron temperature \( T_e \), plasma (or electron) density \( n_e \), and plasma potential in order to ensure reproducible sensitivity factors for different elements. In the present study the fundamental dependences of \( T_e \) and \( n_e \), on adjustable experimental parameters have been established on the first INA3 combined SNMS–secondary ion mass spectrometer system. The results could be explained semiquantitatively by means of the charge carrier and power balances of the plasma. The INA3 system features two measurable parameters for plasma characterization: the floating potential \( U_p \) of an insulated Langmuir probe and the current \( I_p \) measured on a second negatively biased probe. Unique relations could be determined between \( U_p, I_p \) and \( T_e, n_e \sqrt{T_e} \), respectively, as predicted by plasma theory. Furthermore, the variation of \( T_e \) and \( n_e \) as a function of discharge burning time was measured in order to investigate warm-up effects which were found to affect the residual gas suppression efficiency of the system. A detailed study of residual gas influence by adsorption and resputtering from the sample surface showed evidence for a significant reduction of the detection sensitivity of reactive elements like C, N, and O, which may occur on samples with high sticking probabilities for residual gas components.

I. INTRODUCTION

Electron gas secondary neutral mass spectrometry (SNMS) has been proposed as a tool for quantitative surface and in-depth analysis of solids.\textsuperscript{1,2} In the past decade the detection sensitivity and depth resolution of the method have been continuously improved and were demonstrated on a variety of application examples.\textsuperscript{3–10} Very recently (1986), a commercially available SNMS system has been introduced by Leybold–Heraeus (LH), thus making the method available to a large number of potential users and initiating a second test phase of its analytical capabilities. The present study has been performed on the first LH INA3 combined SNMS–secondary ion mass spectrometry (SIMS) system.

In SNMS, neutral particles sputtered from the investigated sample surface by noble gas ion bombardment traverse a special low-pressure rf plasma, the electron component of which serves as a hot Maxwellian electron gas. The sputtered neutral particles are postionized with efficiencies of the order of \( 10^{-2} \) (Ref. 11) by electron impact and are subsequently mass analyzed in a quadrupole based mass spectrometer. Since the sputtering and ionization processes are decoupled, the technique is anticipated to show greatly reduced matrix effects in respect to SIMS and the sensitivity factors \( D_X^0 \) for different elements \( X \) are expected in a first approximation to be apparatus constants determined only by the plasma conditions. Hence, the quantification features of SNMS depend strongly on detailed knowledge and more important, the stability and reproducibility of the essential parameters, e.g., the electron temperature \( T_e \), and the plasma (or electron) density \( n_e \) in the rf discharge. The present study is intended to show the dependence of these values on adjustable system parameters as well as to investigate inevitable influences of experimental conditions on their stability.

II. INSTRUMENTATION

The scheme of the experimental setup used in the INA3 SNMS system is shown in Fig. 1. (Only the parts essential for the operation of the rf plasma are shown.) The electrodeless low-pressure noble gas discharge is excited inductively by means of a single-turn excitation coil which is connected to a 27.1-MHz rf generator. A superimposed static magnetic field \( B \) of the order of 20 G (perpendicular to drawing plane in Fig. 1) allows operation at or near electron cyclotron

![Fig. 1. Experimental setup of the plasma chamber of the LH INA3 sputtered neutral mass spectrometer.](image-url)
wave resonance condition which is essential in order to achieve sufficiently high plasma densities at low discharge pressures. The discharge chamber is a ceramic cylinder of 15-cm diameter and 10-cm height which is closed on both sides by stainless-steel walls, one of which carries the sample mount and Langmuir probe housing. The inner surface of the ceramic is protected against inevitable metal deposition by a disposable Pyrex glass cylinder. In order to reduce heavy wall sputtering and, hence, heavy metal deposition on this cylinder occurring particularly in the plasma region indicated as B, we covered the metal surfaces of the sample mount and Langmuir probe housing by pieces of Pyrex tubing as well. In connection with additional shielding of the remaining metal surfaces with Ta-sheet metal (low sputter yield) this yielded an increase of the operation time of the glass cylinder from approximately two weeks to several months. During normal operation the plasma chamber is connected to the turbomolecular pumped analysis chamber only by two small orifices. The discharge pressure is maintained dynamically and monitored by an ionization gauge in a separate side chamber. Measurements of the pressure ratio between plasma and analysis chamber and calculation of orifice conductances indicated a factor of 2.1 between the plasma ion gauge reading and the actual discharge pressure.

The plasma conditions are monitored by means of two cylindrical Langmuir probes (3-mm-long, 0.5-mm-diam Mo wire). In order to allow accurate characterization of the interesting plasma region between sample and detection system (A in Fig. 1) we extended the probes from their original position (dashed in Fig. 1) into the target plane. The sample is sputtered either by noble gas ions extracted directly from the plasma or by an ion beam from an external ion gun. The sputtered neutral particles, which are postionized while traversing the plasma, approach the subsequent ion optics with their original energy distribution superimposed on the plasma potential variation along their path. Since residual gas ions originally have thermal energies, their energy distribution essentially reflects the plasma potential distribution alone. As a consequence residual gas ions can be discriminated effectively by energy dispersive elements in the ion optics.

III. RESULTS AND DISCUSSION

A. Floating potential and probe current

One of the two measurable parameters provided by LH is the floating potential of a Langmuir probe versus ground. The value of this voltage \( U_p \) represents the plasma potential difference between the location of the probe and the reference electrode, e.g., the grounded wall of the plasma container. Assuming a spatial variation

\[
U(z,r) = f(z,r)kT_e, \tag{1}
\]

\( (U_c: \text{plasma potential with respect to the center of the discharge; } z: \text{coordinate along the cylinder axis with } z = 0, \) \( r = 0 \text{ being the center of the cylinder}, \) \( f(z,r) \) the floating probe voltage is expected to be given by

\[
U_p = \beta kT_e, \tag{2}
\]

with

\[
\beta = f(1/2,R) - f(z_p,r_p) \tag{3}
\]

\( (l,R:\text{plasma cylinder length and radius; } z_p, r_p: \text{probe coordinates}), \) \( f(z,r) \) thus be determined only by \( T_e \) and independent of \( n_e \). The experimental dependence of \( U_p \) on \( T_e \) is shown in Fig. 2 for our system. The values of \( T_e \) as well as all other \( T_e \) and \( n_e \) values reported in the present work have been determined from Langmuir probe curves using the theory for cylindrical probes developed by Langmuir. As can be seen, the observed relation is not linear as predicted by Eq. (2), thus indicating that \( f(z,r) \) is not independent of \( T_e \). Since in the present experiment \( T_e \) was varied by a variation of the discharge pressure between \( 8 \times 10^{-4} \) and \( 4 \times 10^{-3} \) mbar, the density distribution in the Ar plasma is governed by a free flight of the ions to the wall in the low-pressure region \( (\lambda_{Ar,Ar} \approx 10 \text{ cm}) \) and ambipolar diffusion in the high-pressure case \( (\lambda_{Ar,Ar} \approx 3 \text{ cm}) \). The theory for both cases yields significantly different plasma potential distributions \( f(z,r) \) and hence \( \beta \) in Eq. (2) cannot be assumed constant. The results shown in Fig. 2 manifest, however, that \( T_e \) can be estimated from \( U_p \) within an accuracy of \( \pm 10\% \).

The second measurable parameter characterizing the plasma conditions is the current \( I_p \) measured onto a negatively biased (\(-80 \text{ V versus ground}) \) Langmuir probe. Neglecting a second-order correction, which is introduced by small variations of the space-charge sheath around the probe for different plasma potentials, this current should be proportional to the ion saturation current density \( j_i^0 \) which can be extracted from the plasma. With

\[
j_i^0 = n_e \sqrt{kT_e/M_i} \tag{3}
\]

\((M_i: \text{mass of the gas atoms and ions}) \) this yields

\[
I_p = n_e \sqrt{T_e}. \tag{4}
\]

Figure 3 shows the measured probe current versus the right-hand side of Eq. (4) using \( n_e \) and \( T_e \) as determined from Langmuir probe curves. The predicted linear relation is con-

---

**Fig. 2.** Relation between voltage \( U_p \) of insulated Langmuir probe vs ground and electron temperature \( T_e \) in the rf plasma for two different rf-power levels \( P_G \).
firmed by the experimental result. Hence, once $T_e$ has been determined from Fig. 2, $n_e$ can be estimated from Fig. 3 within an accuracy of $\pm 10\%$, thus allowing a complete characterization of the plasma conditions for a particular SNMS analysis.

**B. Dependences of plasma properties on experimental parameters**

Figure 4 shows the experimentally observed variation of $T_e$ and $n_e$ with the discharge pressure $p$. The results essentially agree with previously published data on similar discharges. The obtained pressure dependences can be understood in a simple manner by considering two balance equations of the plasma. The charge carrier balance is given by

$$n_e n_e \alpha_i(T_e) V = n_e^2 \alpha_{rec}(T_e) V + n_e A \sqrt{kT_e / M_i},$$  

(5) $\hspace{1cm}$ (V: volume; A: wall surface of the discharge container). The left-hand side of Eq. (5) describes the electron–ion pair production rate determined by the ionization rate constant $\alpha_i$ and the gas density $n_e$. The first term on the right-hand side describes volume recombination and is negligible due to the low ionization fraction of the plasma ($\approx 10^{-3}$), whereas the second term denotes the wall loss of ions. Hence, the pressure dependence of $T_e$ is given by

$$p / kT_e = n_e / \sqrt{A / \alpha_i(T_e)},$$  

(6) $\hspace{1cm}$ the proportionality constant being determined only by $M_i$ and the value of $A / V$. Calculating $\alpha_i$ for electron impact ionization according to Lotz’s cross-section function, Eq. (6) yields the dashed curve in Fig. 4 which agrees reasonably with the experimental data in the low-pressure region. No explanation can be given at this point for the deviation at the high-pressure end.

The power balance is given by

$$P_{rf} / A = j_e e_0 (E_e + e_0 U_{PL-W}) + j_i e_0 (E_{ei} - e_0 U_{PL-W}).$$  

(7) $\hspace{1cm}$

The left-hand side of Eq. (7) denotes the rf power absorbed by the plasma. The first term on the right-hand side describes the ion portion of the energy loss to the container wall which is determined by $j_i$, the ionization energy $E_i$, and the Langmuir sheath voltage $U_{PL-W}$. According to quasineutrality in the plasma, $U_{PL-W}$ always adjusts so that the ion and electron currents to the wall are equal and electrons with energies smaller than $e_0 U_{PL-W}$ are repelled into the plasma. The second term describes the electron portion of the wall energy loss with $E_{ei}$ being the average electron energy, which is calculated by averaging over the Maxwellian electron energy distribution from $e_0 U_{PL-W}$ to infinity. Combination of Eqs. (3) and (7) yields the following:

$$n_e = \frac{P_{rf} e^{-1/2} \sqrt{M_i}}{A \sqrt{kT_e} \left[ E_e + (1/2 + C) kT_e \right]},$$  

(8) $\hspace{1cm}$

where $C = U_{PL-W} / kT_e = 1 \ln(M_i / 2 \pi m_e) = 4.68$ for Ar. Assuming $P_{rf}$ to be constant, $n_e$ can be calculated from Eq. (8) using the experimentally determined pressure dependence of $T_e$ from Fig. 4. The results were normalized to the respective $n_e$ at $p = 3.8 \times 10^{-3}$ mbar. They are represented by the dashed curves in Fig. 4 and found to agree reasonably well with the experimental data.

Equation (8) also suggests that the plasma density should vary roughly proportionally to the rf-generator power $P_{rf}$. The experimentally measured power dependence of $n_e$ is indeed linear up to $P_{G} \approx 175$ W ($n_e = 0.16 P_{G} / W \times 10^{16}$ cm$^{-3}$). Since $P_{G}$ is the output of power of the rf generator rather than the actually absorbed power $P_{rf}$, at higher $P_{G}$ levels deviations occur which are probably due to increasing rf
losses in this region. Furthermore, the theory predicts $T_e$ to be independent of $P_e$ which is confirmed by the experimental results shown in Fig.4.

The dependence of $T_e$ and $n_e$ on the magnetic field current $I_M$ is shown in Fig. 5. As can be seen, $T_e$ varies only by 14% in the investigated $I_M$ range. Combining this result with Eq. (4), the probe current $I_p$ ($I_M$) directly represents the density variation $n_e$ ($I_M$). The respective curves shown in Fig. 6(b) for three different rf power levels agree reasonably well with previous measurements.13,19 The abrupt breakoffs in the high and low $I_M$ region are probably due to a much stronger coupling between rf oscillator and load circuit compared to the arrangement used in Refs. 13 and 20. The resulting stronger pulling effects on the oscillator induced by load changes lead to a breakdown of the ring discharge in these regions. Because $T_e$ is only weakly dependent on $I_M$ (Fig. 5), the variation of $U_p$ as a function of $I_M$ observed in Fig. 6(a) can only be ascribed to significant changes of the density and potential distribution throughout the plasma chamber. A similar effect has been demonstrated in Ref. 20. This means that variation of $I_M$ (i) changes the relation between $T_e$ and $U_p$ shown in Fig. 2 and (ii) simultaneously changes $n_e$. Hence, we conclude that the appropriate way to reproduce plasma conditions is to first reproduce $U_p$ (and $T_e$) by variation of $p$, $I_p$ (and $n_e$) can be reproduced by a subsequent variation of $P_e$ which leaves $U_p$ and $T_e$ essentially unchanged. $I_M$ should be adjusted only once to or near the maximum $I_p$ (see Fig. 5) and left untouched afterwards.

C. Warm up and stability of the plasma

Detailed knowledge of initial warm up and long-term changes of the plasma conditions are of great importance for doing useful analytical work with SNMS. Hence, the variation of $T_e$ and $n_e$ as a function of discharge burning time has been investigated keeping the instrumental parameters $p$, $P_e$, and $I_M$ constant. The results are shown in Fig. 7. A slight increase of $T_e$ by 4% is observed which is probably due to a
bakeout effect purifying the Ar gas with increasing burning time. Accordingly, $n_e$ is reduced by $\sim 20\%$ during the initial warm-up phase. In contrast to $T_e$, the probe voltage $U_p$ is found to increase by $\sim 20\%$, suggesting a drastic change in the spatial plasma potential distribution. The reason for this effect which is accompanied by an increase of the reflected rf power is probably due to a slight thermal retuning of the rf-load circuit. Since the residual gas suppression of the method is based on energy separation of plasma ions and sputtered particles (see Sec. II), the suppression efficiency is strongly affected by such changes. Accordingly, the resulting intensity $I_{Ar}^0$ of the Ar$^{40}$ peak without sample bombardment increases by roughly a factor of 4 during the warm-up period before going to steady-state conditions.

From the results presented in Fig 7 we have to conclude that a warm-up period of $\sim 100$ min should be allowed after each ignition of the plasma before starting analytical work with the INA3 system. A second point of interest is the alteration of plasma conditions by introducing and changing samples. Figure 8 shows the variation of $T_e$, $n_e$, and $I_{Ar}^0$ induced by two subsequent sample changes from the parking stage. The base pressure in the transfer chamber was $1.5 \times 10^{-7}$ mbar which corresponds to 2–3 h pumpdown time after sample exchange. Although in both cases only slight changes of the plasma conditions occur, the residual gas suppression efficiency is altered by a factor of 3, thus demonstrating again its high sensitivity on the plasma conditions.

D. Residual gas adsorption effects

Although residual gas ions directly extracted from the plasma can be suppressed very efficiently by energy discrimination, this method is not effective for particles which are adsorbed and resputtered from the sample surface. Since according to residual gas spectra the impurity level in the Ar gas is several $10^{-4}$, steady-state coverages ranging from $\sim 100$ ppm to several at. % can be estimated for reactive gases with high sticking probabilities assuming sputter yield values of 1 and 0.1 for bombarding energies of 2000 and 100 eV, respectively. On suitable samples this effect may introduce a severe restriction of the quantification and detection limits for elements like C, N, and O. A good example is given by the analysis of high-purity tungsten where others$^{21}$ observed high-intensity components at mass 12 and 28 in the mass spectrum, tentatively attributed to CO adsorption. Tungsten has a sticking probability close to unity for CO.$^{22}$ Figure 9 shows the SNMS intensities of C, O, W, and WC as a function of bombarding energy. While the W signal increases by almost three orders of magnitude between 100 and 2000 eV, the C and O intensities remain essentially constant as expected for steady-state equilibrium of adsorbed

**Fig. 8.** Variation of (a) electron temperature $T_e$ and density $n_e$ in the rf plasma and (b) residual gas SNMS Ar intensity $I_{Ar}^0$ without sample bombardment as a consequence of sample exchange. The origin of the time axis is given by the ignition of the discharge. At the times marked by dashed lines a new sample was introduced from the parking stage (base pressure $1.5 \times 10^{-7}$ mbar) into the plasma chamber.

**Fig. 9.** Bombarding energy dependence of SNMS C, O, WC, and W signal obtained from a MARZ grade tungsten sample. The open and closed symbols represent data taken before and after purifying the plasma gas by means of Ti sublimation, respectively.
and sputtered flux. For further evidence a Ti–W filament was introduced into the plasma chamber in a position covered by the sample mount housing (see Fig. 1). By Ti sublimation onto the water-cooled sample mount block, the CO peak in the residual gas spectrum could be reduced by roughly a factor of 2. Accordingly, the SNMS intensities of C, O, and WC were reduced by essentially the same factor, while the W intensity remained unchanged. Considering the relative sensitivity factors $D_\text{Ti}/D_\text{W}$ as measured on a W–C standard, \textsuperscript{23} we estimate as the worst case detection limits for C determined by residual gas adsorption to be 1.7 at. %, 0.18 at. %, and 400 ppm for bombarding energies of 100, 500, and 2000 eV, respectively. We feel that in addition to Ti sublimation the effect could be largely reduced by cooling the sample mount block with liquid nitrogen.

**IV. CONCLUSIONS**

Looking for a guideline for the reproduction of plasma parameters in SNMS, correspondence between the measurable parameters $U_p$, $I_p$, and the electron temperature $T_e$ and density $n_e$ can be established within an accuracy of $\sim 10\%$. In agreement with previous results $T_e$ is found to decrease with increasing discharge pressure $p$ while at the same time $n_e$ increases. $T_e$ can be shown to be essentially independent of the rf-generator output power $P_G$ while $n_e$ varies roughly proportional to $P_G$. This decoupling permits a separate reproduction of $T_e$ and $U_p$ by adjustment of $p$, and subsequently of $n_e$ and $I_p$ by adjustment of $P_G$. A detailed study of warm-up effects suggests to allow the system at least 100 min after plasma ignition to reach thermal equilibrium before starting analytical work.

It can be shown that despite very effective residual gas suppression SNMS results may still be affected by adsorbed and resputtered residual gas particles. The effect represents a significant restriction of detection sensitivity for reactive gases which can only be overcome by increased pumping speeds for reactive species in the plasma chamber. A possible way to achieve this goal involves the introduction of a Ti filament as well as a liquid-nitrogen-cooled surface into the plasma chamber.

**ACKNOWLEDGMENTS**

The author is greatly indebted to Dr. W. Reuter and M. Kopnarski for valuable discussions and their continuous interest in the present work.

\textsuperscript{a} Present address: Department of Physics, University of Kaiserslautern, Federal Republic of Germany.


\textsuperscript{19} W. Lotz, Z. Phys. 206, 205 (1967).


\textsuperscript{21} W. Reuter (private communication).
