Fresenius J Anal Chem (1995) 353:510–513

Fresenius' Journal of Analytical Chemistry

High resolution depth profiling of non-conducting samples with SNMS

W. Bock, M. Kopnarski, H. Oechsner

Fachbereich Physik und Institut für Oberflächen und Schichtanalytik, Universität Kaiserslautern, D-67663 Kaiserslautern, Germany

Received: 10 August 1995 / Accepted: 14 August 1995

Abstract. Beat-like signal modulations in sputter depth profiles of multilayer structures are shown to enable an estimation and the optimization of the homogeneity of the sputter erosion process. Using W-Si multilayer structures of 69 doublelayers with a thickness of 40 Å, it is shown that the high-frequency mode (HFM) of electron-gas SNMS (e^--gas SNMS) for the analysis of insulators provides the same high depth resolution as the conventional direct-bombardment mode (DBM) of this technique.

Introduction

Secondary neutral mass spectrometry with electron-gas postionization has been shown to be a suitable technique for the quantitative analysis of the composition of surfaces and thin films, especially when high depth resolution is required [1, 2].

A recent methodical development of e^--gas SNMS is the so-called high frequency mode HFM for the analysis of electrically insulating samples [3, 4, 5, 6]. In comparison to the established modes for the analysis of non-conducting samples, the separate and the external bombardment mode (SBM and EBM), [7, 8]), i.e. techniques that use an ion gun for sputter erosion, the HFM applies the plasma as sputter-ion source similar to the conventional direct bombardment mode DBM.

The special advantage of the DBM is its high depth resolution by establishing low bombarding energies. Crater effects can be avoided by choosing the bombarding voltage U_b for a given distance D between the sample and an aperture in contact with the plasma (Fig. 1) very accurately in order to obtain a plane plasma boundary. According to the $d \propto U^{3/4}$ law [1], the plasma boundary is bent out- or inward leading to an inhomogeneous distribution of the bombarding ion current when U_b is too low or too high. The developing sputter crater will then have a concave or convex profile, respectively (Fig. 1).

The present paper aims to demonstrate that the HFM provides the same high depth resolution capabilities as the DBM.

Correspondence to: H. Oechsner

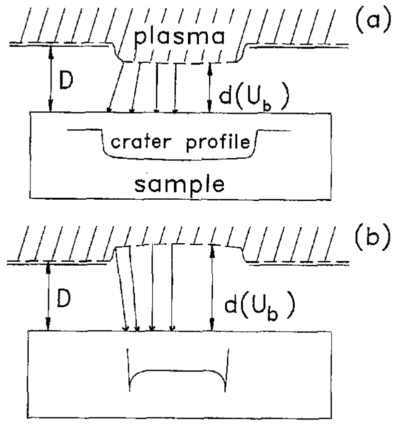

Fig. 1 a, b. Schematic illustration of the deformation of the plasma boundary for **a** too low and **b** too high bombarding voltages and the resulting crater profiles

The High Frequency Mode

The setup for the HFM is in principle the same as for the DBM [1]. However, to avoid a charging of insulating samples during sputtering, a high frequency (some 100 kHz up to 1 MHz) rectangular shaped voltage with a total amplitude U_{HF} is now applied to the sample (Fig. 2) instead of a DC voltage via a conducting sample holder. During the part T^- of the HF cycle the sample is sputtered by the extracted plasma ions and accumulates charge. This charge is compensated in part T^+ of the cycle, when the bombarding voltage is switched off and electrons from the plasma can reach the specimen. The behavior of the potential U(t) at the sample surface during the HF-period can be described by [5]:

$$\dot{U} = \frac{1}{C}\,[I_i^s + I_e^r\,U(t))] \text{ for } U(t) < U_{pl} \tag{1}$$

where C is the capacity of the sample arrangement and U_{pl} the (constant) plasma potential against a grounded electrode. I_i^s is the ion saturation-current given by

$$I_i^s = A \cdot n_i \cdot e_0 \cdot \alpha \cdot \sqrt{\frac{kT_e}{m_i}}$$

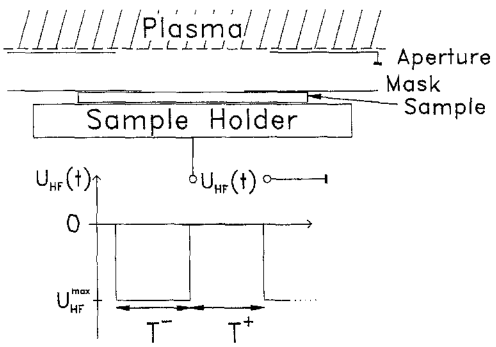

Fig. 2. Arrangement for the high frequency mode HFM of e-gas SNMS

A is the area of the aperture determining the ion extraction section, $n_i = n_e = n$ the plasma density, e_0 unit charge, T_e the electron temperature and m_i the ion mass. α is a factor in the order of 0.5 to 0.8 which accounts for the variation of n and the potential inside the plasma [9].

I_e^r in Eq.(1) is the electron retardation-current given by

$$I_e^r = I_e^s \cdot e^{-\eta(U_{Pl}-U(t))} = -A \cdot n_e \cdot e_0 \cdot \sqrt{\frac{kT_e}{2\pi m_e}} \cdot e^{-\eta(U_{Pl}-U(t))}$$

where I_e^s is the electron saturation current and $\eta = e_0/kT_e$ (m_e electron mass)

The differential Eq.(1) is solved by

$$U(t) = \begin{cases} U_{pl} - \eta^{-1} \cdot \ln\left[-\frac{I_s^e}{I_i^s}\left(1 - e^{\frac{\eta I_i^s}{C} \cdot t}\right) + e^{\eta(U_{Pl}-U_{HF})}\right] + \\ + \frac{I_i^s}{C} \cdot t; \quad U(t) < 0, T^- \\ U_{pl} - \eta^{-1} \cdot \ln\left[-\frac{I_s^e}{I_i^s}\left(1 - e^{\frac{\eta I_i^s}{C} \cdot t}\right) + e^{\eta(U_{Pl}-U_{HF})}\right] + \\ + \frac{I_i^s}{C} \cdot t; \quad 0 \le U(t) \le U_{pl}, T^+ \end{cases} \qquad (2)$$

An example for the time dependent variation of the surface potential U(t) is given in Fig. 3.

During the ion bombarding interval T^- the charge built up at the sample (U_{ch}) reduces the effective bombarding voltage $U_b = |U_{HF}| + U_{Pl}$ to a value $U_b' = U_b - U_{ch}$ at the end of T^-. U_{HF} becomes zero at the beginning of T^+, and the surface potential rises by this value. U(t) at this point is therefore given by U_{ch}. This means, the higher U_{ch}, the higher is the current of plasma electrons which now starts to flow. If $U_{ch} > U_{pl}$, even an electron saturation current I_e^s is drawn by the sample, reducing its potential very fast (some 10^{-8} s) to a value below U_{pl} because I_e^s is about two orders of magnitude above the ion saturation current I_i^s. For $U_{ch} < U_{pl}$ both an electron retardation current I_e^r and the ion saturation current I_i^s arrive at the sample surface, shifting its potential to the floating potential U_{fl} (i.e. the potential of an insulated probe in the plasma), where $I_i^s = I_e^r$.

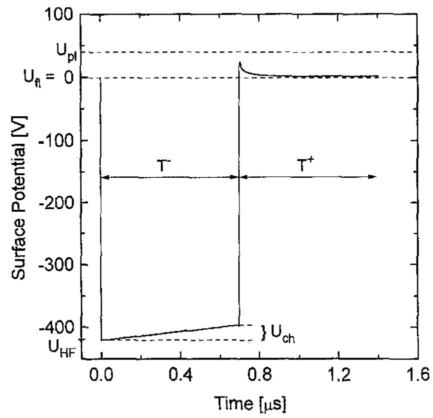

Fig. 3. Potential of the sample surface according to Eq.(2) for $U_{ch} < U_{HF}$

For $U_{ch} << |U_{HF}|$ the electron retardation-current in Eq.(1) can be neglected and U(t) is given by

$$U(t) = U_{HF} + \frac{I_i^s}{C} \cdot t \qquad (3\,a)$$

and U_{ch} at the end of T^- is

$$U_{ch} = \frac{I_i^s}{C} \cdot \frac{\gamma}{\nu_{HF}} \qquad (3\,b)$$

with $\gamma = T^-/(T^+ + T^-)$. ν_{HF} is the frequency of the applied rectangular HF voltage. The higer I_i^s or γ and the lower C or ν_{HF} are, the higher will be U_{ch}. Since I_i^s and C are constants of the apparatus and the sample, respectively, charging can be reduced by increasing ν_{HF} or reducing γ.

For samples with a low capactiy (e.g. for oxidic glasses with a low dielectric constant ε), a charge build-up cannot be completely avoided even for very high values of ν_{HF}. Then the applied voltage, and therefore the distance d between the plasma boundary and the sample surface do not remain constant during T^-. Since the depth resolution depends strongly on the shape of the plasma boundary, the question arises, if it is possible to obtain good depth resolution with the HFM at all.

Experiment

Depth analysis of a multilayer structure is a good possibility for checking the depth resolution during sputter-profiling. In the present study we used a W-Si multilayer structure with 69 double layers of 40 Å each, deposited on crystalline silicon. In order to form a non-conducting sample, the multilayer specimen was insulated against the sample holder by a glass slide (0.4 mm thick, $\varepsilon = 5.8$ at 1 MHz). A circular mask covering the sample was at the same potential as the sample surface. The measurements were carried out in a Leybold INA3 e^- gas SNMS instrument [2].

A typical intensity versus erosion-time profile of such a multilayer is shown in Fig. 4. A striking feature of this profile is the modulation of both the W and Si signal superimposing the periodical variation of the signals from the individual layers. The long range variations can be referred to an inhomogeneous bombarding current, resulting

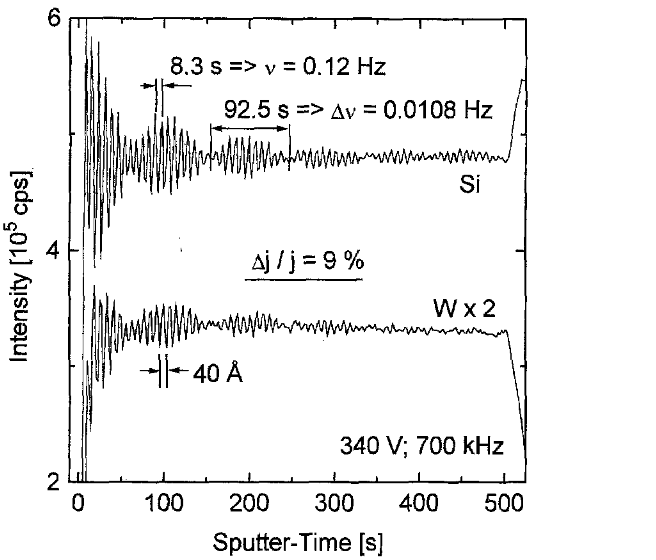

Fig. 4. Intensity vs. sputter-time profiles for an insulated W-Si multilayer with 700 kHz and $\gamma = 0.5$. The HF amplitude was 340 V

in different erosion rates at different parts of the crater. Then, the superposition of contributions from different crater sites results in a beat-like modulation of the signal oscillations from the individual layers. Assuming only two different ion current densities j_1 and j_2 as a rough approximation (e.g. in the center and at the edge of the crater), the "beat frequency" $\Delta\nu$ of the long range signal modulation is given by

$$\Delta\nu = \nu_1 - \nu_2 \sim \frac{j_1 - j_2}{a} = \frac{\Delta j}{a} \quad \text{a: doublelayer spacing.} \qquad (4)$$

Hence, the inhomogeneity of the bombarding current can be expressed as

$$\frac{\Delta j}{j} = \frac{\Delta\nu}{\nu} \qquad (5)$$

For the respective depth profile measurements shown in Figs. 4 and 5 HF-voltages of different amplitudes U_{HF} have been applied at a constant distance of D = 2 mm between the plasma aperture and the sample. ν_{HF} was always 700 kHz, and $\gamma = 0.5$. Starting with $U_{HF} = 340$ V (Fig. 4) an increase of the bombarding voltage by steps of 10 V leads to an improved homogeneity of the sputter erosion. The best result for the chosen step width was achieved for 420 V (Fig. 5 a). At higher voltage (440 V) the erosion homogeneity deteriorates again (Fig. 5 b).

According to that the optimum HF-voltage must be about 420 V for $\nu_{HF} = 700$ kHz and the actual sample configuration. This is in contrast to corresponding DBM measurements, where the optimum voltage was found to be around 300 V. The investigation of this discrepancy will be the subject of further experiments. It is very likely that the higher optimum voltage in the HFM is connected with charging effects that will reduce the bombarding voltage to a lower value. This assumption is supported by a calculated value of $U_{ch} = 80$ V according to Eq. (3 b), that would reduce the effective U_{HF} to a value near 300 V.

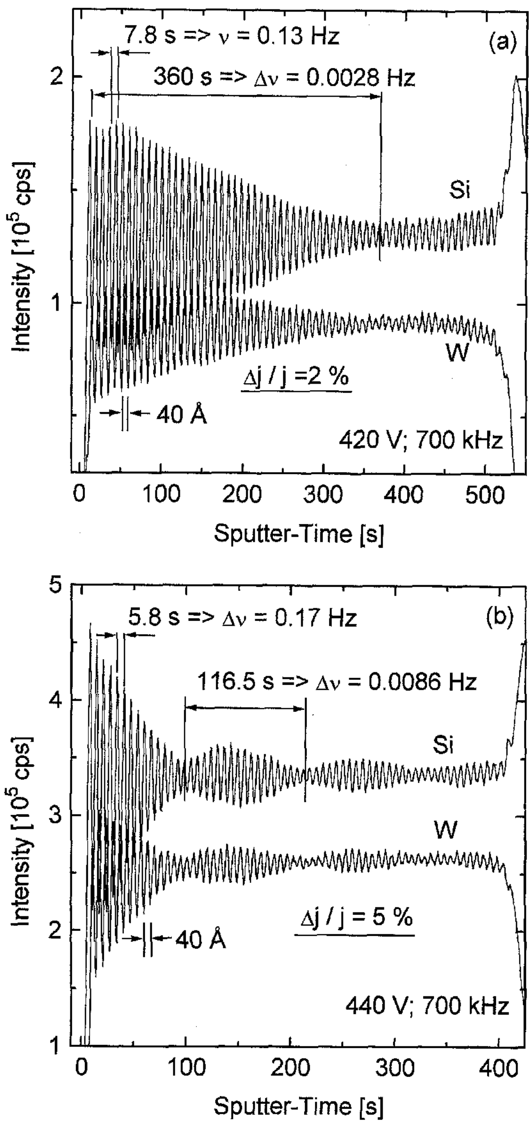

Fig. 5 a, b. As in Fig. 4, but for HF-voltages of **a** 420 V and **b** 440 V

Conclusion

It was demonstrated that the high-frequency mode of electron gas SNMS enables the analysis of insulators with a depth resolution as good as obtained with the direct-bombardment mode for conducting samples. A very easy and fast method to check and optimize the depth resolution determined by the homogeneity of the sputter erosion is the analysis of multilayer structures. For practical performance, we propose to mount thin conducting multilayer samples onto the insulating sample to be analysed. Then the capacity of the non-conducting sample will determine that of the whole structure, and the U_{HF}-value for optimum depth resolution of the multilayer will also apply to the insulator.

References

1. Stumpe E, Oechsner H, Schoof H (1979) Appl Phys 20:55
2. Jede R, Peters H, Dünnebier G, Ganschow O, Kaiser U, Seifert K (1988) J Vac Sci Technol A6(4):2271
3. Vogelgesang A (1988) Diploma Thesis, Universität Kaiserslautern
4. Heckmann B (1990) Diploma Thesis, Universität Kaiserslautern
5. Friedrich S (1993) Diploma Thesis, Universität Kaiserslautern
6. Oechsner H (1993) Appl Surf Sci 70/71:250
7. Müller KH, Seifert K, Wilmers M (1985) J Vac Sci Technol A3:1367
8. Geiger JF, Kopnarski M, Oechsner H, Paulus H (1987) Mikrochim Acta I:497
9. Oechsner H (1970) Z Phys 238:433