

X-ray photoelectron spectroscopy of hafnium nitride

E. BRUNINX, A. F. P. M. VAN EENBERGEN, P. VAN DER WERF, J. HAISMA
Philips Research Laboratories, PO Box 80 000, 5600 JA Eindhoven, The Netherlands

The N-1s line of hafnium nitride layers prepared under various chemical and physical conditions has been examined by X-ray photoelectron spectroscopy at 30 and 575°C as well as intermittently during sputter profiling at room temperature.

1. Introduction

Hafnium compounds are materials with such extreme properties that hafnium carbide is the most refractory binary compound known and hafnium nitride is the most refractory of all nitrides, having a melting point of 3305°C. Besides this, hafnium binary compounds have excellent mechanical properties [1, 2] and hard metal tools covered with a thin layer of it are well known for this reason. Hafnium nitride has a superior hardness with respect to the other carbides and nitrides at higher temperatures, as was demonstrated by the transparent turning of optical glasses at elevated temperatures on a lathe [3, 4]. It was shown that some optical glasses were turnable (like metals with a continuous chip) at elevated temperatures (up to 700°C, depending on the type of glass) if machined by a hard metal tool covered with a carbide or nitride binary compound layer. In this series of experiments it was found that hafnium nitride is one of the best tool coverages for this purpose. With optimized engineering it was even possible to produce a transparent surface state (i.e. free from light scattering).

Polycrystalline hafnium nitride can be prepared by pure chemical means, as a thin layer by chemical vapour deposition (CVD) or by reactive sputter deposition. For the CVD method the substrate temperature (T_s) is normally kept high — above 1000°C — in order to obtain thin layers of X-ray diffraction pure hafnium nitride, well adhered to the substrate.

It was the purpose of this study to investigate a number of samples by X-ray photoelectron spectroscopy (XPS) more quantitatively, for verifying the composition of various hafnium nitride layers prepared at lower temperatures. The following variants therefore were studied:

(a) HfN as a powder, chemically prepared by two different manufacturers (preparation temperatures above 1000°C);

(b) HfN reactively sputter-deposited on nickel ($T_s \approx 400^\circ\text{C}$) measured at 30 and 575°C;

(c) HfN reactively sputter-deposited on nickel ($T_s \approx 400^\circ\text{C}$) in which hafnium and nitrogen are measured as a function of sputter depth at room temperature.

In order to verify the observed binding energies and

more specifically the N-1s line shape, a few additional measurements were made on titanium nitride on nickel substrates, titanium nitride being prepared by sputter deposition ($T_s \approx 400^\circ\text{C}$). Moreover $\text{Ba}(\text{NO}_3)_2$ was measured at low and high temperature in order to check the presence or absence of N_xO_y groups.

2. Experimental details

2.1. Preparation of samples

Powders of hafnium nitride (99.8% pure, 325 mesh) were bought from Cerac (Menomonee Falls, Wisconsin, USA). Another powder (called Philips) was made in our laboratories by nitriding hafnium powder at 1400°C in nitrogen. This powder was examined by X-ray diffraction and the spectrum showed only peaks of hafnium nitride. From a chemical analysis it was deduced that the powder contained about 0.5 wt % HfO_2 .

The sputter-deposited hafnium nitride layers were obtained in an Edwards r.f. sputtering system, having a facility of two electrodes well separated and operating simultaneously in order to deposit two types of material under the same experimental conditions (see Fig. 1a).

The vacuum chamber, a Pyrex glass cylinder of 30 cm diameter and 36 cm height, was evacuated by an oil diffusion pumping system. The ultimate pressure was in the 10^{-6} torr range, while during sputtering the pressure of the pure nitrogen was 5×10^{-3} torr. A hafnium nitride target of 75 mm diameter (Demetron) was placed on the r.f. electrode; in some experiments we started from a hafnium metal target. The maximum achievable power of the r.f. generator was 5 kW at a frequency of 13.56 MHz. About 30% of the maximum power was used in the experiments. An axial magnetic field of 10^{-2} T (100 Oe) was used to increase the plasma density.

For the deposition of hafnium nitride on nickel (to have a substrate which is basically oxygen-free) we used simultaneously a hafnium nitride as well as a hafnium target in a geometrical arrangement as shown in Fig. 1a, the separation of substrate and target being 3 cm. The deposition rate of hafnium nitride at a chosen power input of 1.5 kW was 2 nm min^{-1} and the thickness of the investigated hafnium nitride layers was about 100 nm.

The titanium nitride layers were made for reasons of

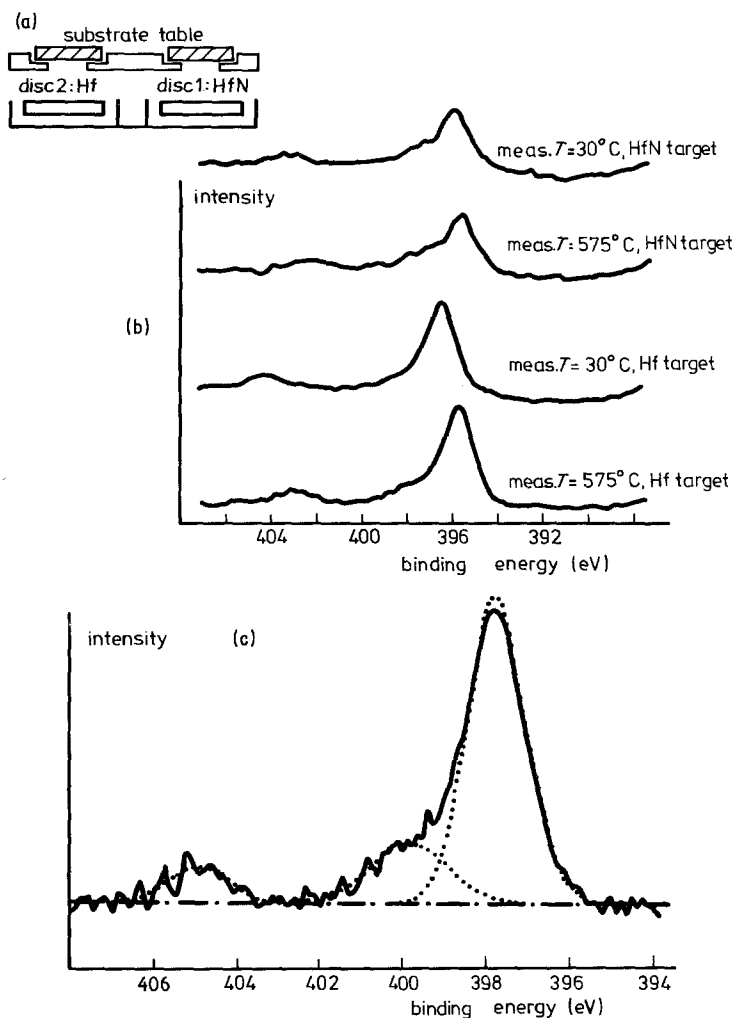


Figure 1 (a) Set-up for sputter deposition from two different targets. (b) N-1s narrow-scan spectra from HfN on nickel measured at 30 and 575°C for samples prepared by sputter deposition from hafnium or HfN targets. (c) Curve-fitting of N-1s line with three Gaussian components (measuring temperature 575°C, hafnium target).

comparison by reactive sputtering in an MRC (Materials Research Corporation) sputter sphere, Model 822 (from Edwards High Vacuum, Crawley, Sussex, UK). A titanium target, 20 cm in diameter, was sputtered off in a pure nitrogen gas at a pressure of 5×10^{-3} torr. The ultimate pressure of the vacuum system was in the 10^{-7} torr range. The substrate-target distance was 4 cm. The r.f. power system consisted of a 1.5 kW r.f. power supply working at a frequency of 13.56 MHz. The sputter rate at 1 kW was 4 nm min^{-1} and the titanium nitride layers on nickel were about 200 nm thick [5].

$\text{Ba}(\text{NO}_3)_2$ was used as a powder pressed into a small disc.

2.2. XPS measurements

All measurements were made with a Leybold-Heraeus LHS-10 electron spectrometer and the spectra were stored in a Canberra multichannel analyser. Survey spectra (0 to 1500 eV, 2048 channels, 0.73 eV per channel) were recorded with a constant retarding factor. In this mode the kinetic energy of the electrons is retarded by a factor of three. The narrow-scan spectra of O-1s (binding energy = 530 eV), N-1s (400 eV), Hf-4d_{5/2} (215 eV) and C-1s (285 eV) were measured by the electron energy analyser with a constant transmission energy of 100 eV. In this mode we measured for the Au-4f_{7/2} line a binding energy of 83.9 eV and a line width of 1.4 eV.

The width of the analysed energy band was about

20 eV for all four elements carbon, oxygen, nitrogen and hafnium (stored in 256 channels; 0.079 eV per channel). The excitation source was unmonochromatized AlK α radiation (30 mA, 10 kV).

The peak area of an element i was converted in concentration by means of the formulae

$$I = K\sigma_{LH}N\lambda$$

$$n_i = N_i / \sum_i N_i$$

where I is the measured net peak area, N is concentration, K is an instrument factor, σ_{LH} is the calculated cross-section for this type of spectrometer [6], λ is the mean free path [7] and n_i is the fractional concentration of element i in the analysed layer.

All samples were analysed without any preliminary cleaning treatment such as sputtering. This was done on purpose since it was not known to what extent chemical composition could be influenced by sputtering. Foils carrying hafnium nitride were screwed on to the standard sample rods; powders were deposited into a small stainless steel cup as evenly as possible. They were then introduced into the sample lock under atmospheric nitrogen pressure and slowly pumped down in order to avoid any blow-up.

The depth profile of the hafnium nitride layer was made by sputtering with an argon beam (4 keV, $6 \mu\text{A cm}^{-2}$, angle of incidence 60°).

Composite photoelectric lines were fitted with Gaussian lines by means of the least-squares method

TABLE I Binding energies and concentrations of HfN powders

| | Source of powder | | Average value | Difference* |
|-----------------------------------|------------------|-------|---------------|-------------|
| | Philips | Cerac | | |
| Binding energy (eV) | | | | |
| Hf-4d5/2 | 215.3 | 215.6 | 215.5 | |
| N-1s, N ₁ | 399.0 | 399.0 | 399.0 | 183.5 |
| N ₂ | 401.8 | 401.9 | 401.9 | 186.4 |
| N ₃ | 406.1 | 406.1 | 406.1 | 190.6 |
| C-1s | 285.9 | 285.9 | | |
| Concentration ratio nitride/oxide | 0.5 | 0.46 | | |

*Difference = average binding energy (N component) – average binding energy (Hf-4d5/2).

[8], based on a routine (E04FBA) taken from the NAG library [9]. A linear background was assumed for all spectra. All nitrogen lines were analysed in this way; oxygen was analysed occasionally. For the carbon and hafnium lines no curve-fitting was undertaken.

Since not all samples were electrically conducting the binding energy of the carbon (including adventitious or spectrometer carbon), hafnium and nitrogen lines are given in the tables below. For comparison with data obtained with other instruments it is more meaningful to consider the differences rather than the absolute values.

3. Results

3.1. HfN powders

The observed binding energies for the Cerac and Philips powders are shown in Table I: there is little difference between the two preparations. The N-1s line consists of three components N₁, N₂ and N₃; the first two can be ascribed to the nitride. The curve-fitting of the N-1s line was difficult due to the poor counting statistics; the uncertainty of the different nitrogen intensities was thus quite large. The O-1s line shape was asymmetric, which points to more than one form of oxygen. No further identification or curve-fitting was attempted.

Assuming that all hafnium is present as HfN and HfO₂, we can estimate the ratio HfN/HfO₂ in the analysed layer. The results in Table I show that the

outer layers of these powders consisted mainly of HfO₂, while bulk analysis (as mentioned earlier) indicated only 0.5% HfO₂. In addition the surface carbon content of these powders is very high, around 60%. More accurate determinations could be carried out by fitted individual components to the hafnium, oxygen and carbon lines. This evaluation is however outside the scope of the present paper.

3.2. HfN on nickel measured at low and high temperatures

Since the surfaces of the powders had rather high oxide and carbon concentrations, all further measurements were done on thin hafnium nitride layers. We examined layers deposited by reactive sputtering from hafnium and hafnium nitride targets on to nickel foil (see Fig. 1a for the set-up).

The layers were measured both at 30 and 575°C. The high-temperature measurements were done in order to bring into evidence any unstable nitrogen compound that might have been present. Examination of the O-1s line measured at the higher temperature could possibly shed some light on the existence of less stable oxygen compounds such as hydroxides or water.

The results are summarized in Table II. The nitrogen intensities were normalized to the line with the lowest binding energy (i.e. the nitride line). For all four samples it appears that the difference in binding energy between Hf-4d5/2 and N-1s is fairly constant. The average energy differences are on the whole 1 to 2 eV smaller than for the powder samples. This difference is significant, because we estimate that the uncertainty in the energy differences is about 0.3 eV at the most. The effect is due to the large amount of oxide present in the powders, which yields a higher binding energy value for the Hf-4d5/2 line. The absolute value of the N-1s binding energies (396.6 eV) is to be compared with the value of 397.6 eV obtained by Steiner *et al.* [10].

Figs. 1b and c shows the N-1s region for all four samples, together with an example of the three nitrogen components fitted with a Gaussian line shape. The full width at half maximum intensity (FWHM) for the most intense nitrogen line is around 1.7 eV; for the

TABLE II Binding energies and concentrations measured at 30 and 575°C for sputter-deposited HfN from hafnium and HfN targets

| | Sputtering target and measuring temperature (°C) | | | | Average value | Difference* |
|-----------------------------------|--|---------|-----------|----------|---------------|-------------|
| | HfN (30) | Hf (30) | HfN (575) | Hf (575) | | |
| Binding energies (eV) | | | | | | |
| Hf-4d5/2 | 213.9 | 214.1 | 213.5 | 213.6 | 213.8 | |
| N-1s, N ₁ | 396.6 | 397.2 | 296.3 | 396.4 | 396.6 | 182.8 |
| N ₂ | 398.4 | 399.2 | 398.4 | 398.5 | 398.6 | 184.8 |
| N ₃ | 403.9 | 404.9 | 403.2 | 403.6 | 403.9 | 189.0 |
| C-1s | 285.9 | 286.6 | 284.7 | 285.0 | | |
| Relative Intensities | | | | | | |
| N-1s, N ₁ | 1 | 1 | 1 | 1 | | |
| N ₂ | 0.32 | 0.19 | 0.23 | 0.28 | | |
| N ₃ | 0.14 | 0.13 | 0.10 | 0.12 | | |
| Concentration ratio nitride/oxide | 0.40 | 1.2 | 0.45 | 0.72 | | |

*Difference = average binding energy (N component) – average binding energy (Hf-4d5/2).

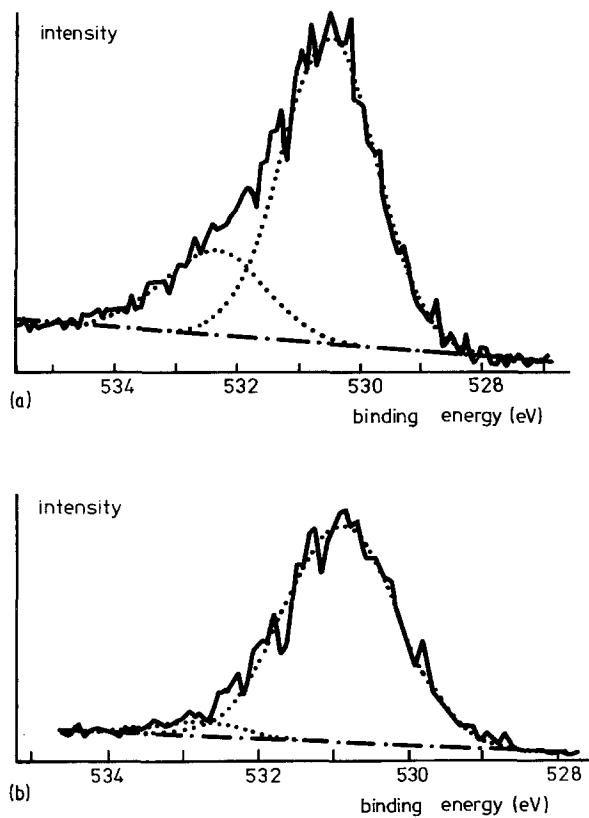


Figure 2 O-1s line with two components measured at (a) 30°C and (b) 575°C.

second line it is somewhat higher at 1.8 to 1.9 eV. The width of the line with the lowest intensity is difficult to determine; it varies between 1.4 and 1.7 eV, with an uncertainty of about 0.2 eV. In the fitting process all parameters such as FWHM, area and peak position were left free. The line-width for these four samples is considerably smaller than for the powders, where it is around 2.5 to 3.5 eV. The smaller oxide content and the somewhat better electrical conductivity of the thin layers on nickel are responsible for this effect. The structure of the N-1s line remains quite unchanged for all four samples.

The oxygen band of the high-temperature measurements shows a decreased intensity (Fig. 2) on the high binding-energy side. This is probably due to a reduction of the water content in the sample. However, there seems to be less hafnium nitride in samples sputtered from a hafnium nitride target.

3.3. HfN sputter profiling experiments

A depth profile was made of hafnium nitride deposited on nickel by sputtering with an argon beam up to a total sputtering time of 1280 sec. The sputter rate was about 0.08 nm in 10 sec. This was measured by means of a Tally step on a highly flat and sputter-deposited hafnium nitride sample. The Hf-4p_{3/2} and N-1s lines were recorded. Curve-fitting was applied only to the N-1s line. The hafnium intensity and the fractional intensities of the fitted N-1s line components were normalized to the intensity measured after 10 sec of sputtering: most of the contaminated top layer was then sputtered off. The data are summarized in Fig. 3.

The intensity ratio N_2/N_1 lies around 0.2 for all sputter times; N_3/N_1 decreases continually. Fig. 4 shows the N-1s line after 10 and 1280 sec of sputtering. The line with a binding energy around 404 eV has completely disappeared, while the structure of the other two lines remains constant. One could perhaps argue that there is an additional nitrogen component around 401 eV, but the poor counting statistics in this region do not justify such an assumption. Disappearance of the N_3 component suggests that this could be some type of plasmon line. Whether it must really be attributed to nitrogen is not entirely clear, since Hf-4p_{3/2} also shows a satellite structure in this energy region.

4. Discussion

Although a few articles have been published describing XPS measurements of various nitrides [10-14] only three of these references show some data on the N-1s line shape [11, 13, 14]. Some of these graphs show clearly an asymmetric shape of the N-1s line.

It has been suggested by Kharlamov and Aleshin [11] that the shoulder at the high binding-energy side of the N-1s line (i.e. N_2) is due to NO. In view of the previous high-temperature measurements and the sputtering experiments we can rule out this possibility. The existence of other N_xO_y groups was also ruled out by measuring $Ba(NO_3)_2$ at room temperature and at 575°C: no N_xO_y compounds could be detected in the hafnium nitride layer.

TiN measured at 30 and 575°C yielded also an asymmetric N-1s line as shown in Fig. 5. Curve-fitting indicated the presence of three components with binding energies of 396, 398.2 and 400.6 eV. The last two

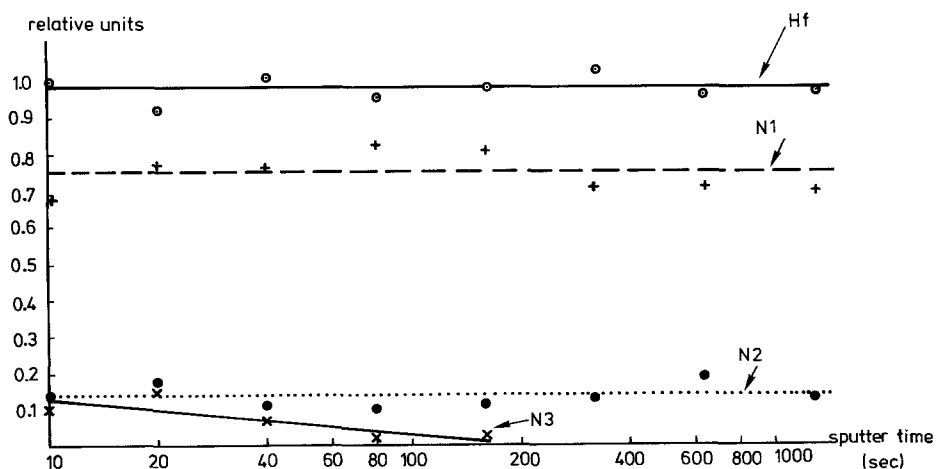


Figure 3 Influence of time of sputtering on Hf-4p_{3/2} intensity and relative intensities of the three N-1s components (all normalized to values at 10 sec).

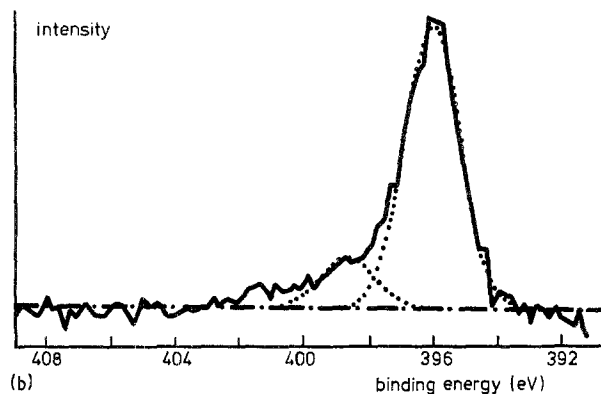
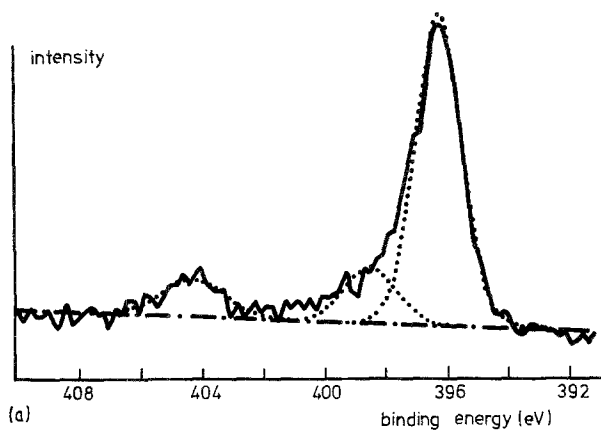


Figure 4 N-1s line from HfN on nickel after (a) 10 and (b) 1280 sec of sputtering.

values are somewhat uncertain, since these two lines can be fitted equally well by one component with a larger FWHM. The third component (at 400.6 eV) lies however distinctly closer to the main nitride line than the third component for hafnium nitride (at 404 eV).

The relative intensity of the component at 398.2 eV is higher than for hafnium nitride: it amounts to about 0.3 to 0.4 for titanium nitride as compared to 0.2 for hafnium nitride.

The structure of the N-1s (nitride) lines does not change drastically when the measurement temperature is raised or the TiN deposition procedure changed. The line-width of the main nitride line is about the same as for hafnium nitride and amounts to 1.7 eV.

Since the hafnium nitride sputter experiments do not show any change in intensity for the N_2 component we may conclude that it is distributed evenly throughout the analysed layer. This was further confirmed by measuring the N-1s line at two different emission angles (off-normal): 0° and 60° . In both cases the relative ratio of the two nitride components (N_1 and N_2) remained unchanged.

It is also unlikely that oxynitrides would be responsible for the N_2 component: at such a high concentration the X-ray diffractogram would reveal their presence.

We believe therefore that some free nitrogen at interstitial sites is responsible for this shoulder [15, 16]. It is not likely, in view of the high melting point of hafnium nitride, that this interstitial nitrogen is released at 575°C .

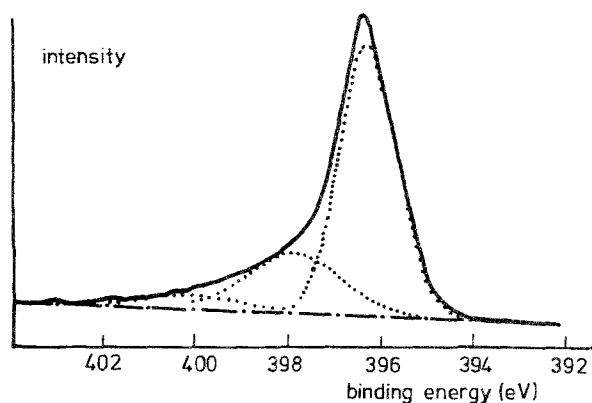


Figure 5 N-1s line fitted with Gaussian components for sputter-deposited TiN. Measuring temperature 575°C .

The stability of hafnium nitride during the sputtering process is not well known. However, in view of the observation that the ratio N_2/N_1 and Hf/N_1 remains constant, we believe that hafnium nitride remains unchanged over the total depth sputtered (9.6 nm). Our observations are opposite to those of Höchst *et al.* [12] who stated (without further experimental evidence) that preferential sputtering occurs for nitrogen in nitrides.

The binding energy of the Hf-4p_{3/2} line shifts about 1 eV to lower values during sputtering. We think that the observed shift in binding energy can be attributed to the decomposition of hydroxides [17].

5. Conclusions

The N-1s line in hafnium nitride, titanium nitride and probably a few other nitrides has a complex structure. This structure was not influenced by high-temperature treatment or different preparation techniques. The presence of N_xO_y groups can also be ruled out.

Sputter profiling of hafnium nitride layers indicated no preferential sputter effects.

Whatever the preparation technique may be, hafnium nitride layers contain (at least at the surface) variable amounts of hafnium oxides. The presence of other undetermined oxygen-containing compounds cannot be ruled out.

References

1. L. E. TOTH, in "Transition metal carbides and nitrides" (Academic Press, New York, 1971) p. 6.
2. A. J. PERRY, B. HAMMER and M. GROESSL, in Proceedings of the 4th European Conference on Chemical Vapour Deposition, Eindhoven, May/June 1983, edited by J. Bloem, G. Verspui and L. R. Wolff (Eindhoven Druk B.V.), p. 70.
3. R. BREHM, K. VAN DUN, J. C. G. THEUNISSEN and J. HAISMA, *Precision Engng* **1** (1979) 207.
4. R. BREHM and J. HAISMA, in Proceedings of the Society of Photo-optical Instrumentation Engineers, Vol. 235, edited by L. Baker and K. Rosenbruch (Bellingham, Washington, 1979), p. 99.
5. P. J. M. VAN DER STRATEN and G. VERSPUI, *Philips Technol. Rev.* **40** (1982) 141.
6. E. BRUNNX and A. VAN EENBERGEN, *Spectrochim. Acta* **38B** (1983) 821.
7. M. SEAH and W. DENCH, *Surf. Interf. Anal.* **1** (1979) 2.
8. A. VAN EENBERGEN and E. BRUNNX, unpublished report (1984).
9. Available from Numerical Algorithm Group, (1984) Oxford, UK.

10. P. STEINER, H. HÖCHST, J. SCHNEIDER, S. HÜFNER and C. POLITIS, *Z. Phys. B* **33** (1979) 241.
11. A. KHARLAMOV and V. ALESHIN, *Neorg. Materialn* **16** (1980) 445.
12. H. HÖCHST, R. BRINGANS, P. STEINER and T. WOLF, *Phys. Rev. B* **25** (1982) 7183.
13. Y. SHULGA, V. TROITSKII, M. AIVAZOV and Y. BORODKO, *Russ. J. Inorg. Chem.* **21** (1976) 1441.
14. V. ALECHIN, A. KARLAMOVA and T. VARTNICHKAYA, *Neorgan. Materialn.* **15** (1979) 677.
15. B. JOHANSSON, J. SUNDGREN, U. HELMERSSON and M. HIBBS, *Appl. Phys. Lett.* **44** (1984) 670.
16. E. RUDY and F. BENESOVSKY, *Monatsh. Chem.* **92** (1961) 415.
17. S. HOFMANN and J. SANZ, *J. Trace Microprobe Techn.* **1** (1982/83) 213.

*Received 25 June 1984
and accepted 29 March 1985*