

Composition and chemical state of titanium nitride films obtained by different methods

J. S. Colligon^a, H. Kheyrandish^a, L. N. Lesnevsky^b, A. Naumkin^c, A. Rogozin^d, I. I. Shkarban^b, L. Vasilyev^c and V. E. Yurasova^d

^aCentre for Thin Film and Surface Research, Department of Electronic and Electrical Engineering, Salford University, Salford M5 4WT (UK)

^bMoscow Aviation Institute, Volokolamskoe Shosse 4, Moscow 125871 (Russian Federation)

^cAnteh Ltd, Krasnokazarmenny per. 6, Moscow 109028 (Russian Federation)

^dPhysics Department, Moscow State University, Moscow 117234 (Russian Federation)

(Received February 14, 1994)

Abstract

Titanium nitride films were obtained by three methods: ion-assisted deposition, deposition using the cathode spot arc discharge system (ion plating) and deposition using a planar magnetron. The resulting films were analysed by X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry. Depending on the preparation conditions, the films were shown to have different composition and different colour (golden, copper-like, or blue). The golden-coloured films, formed by magnetron sputtering, comprise about 95% titanium nitride and about 5% titanium oxynitride. The other samples contain less titanium nitride, especially the blue-coloured films which contain only about 55% titanium nitride, 35% titanium oxynitrides and 10% titanium oxides.

1. Introduction

Titanium nitride is an important material with numerous applications including wear and corrosion-resistant coatings, diffusion barriers in VLSI devices, and decorative coatings. However, in spite of the vast number of publications relating to the deposition of titanium nitride coatings by a variety of techniques such as reactive evaporation, magnetron sputtering and ion-assisted deposition, a detailed and comprehensive study allowing a correlation between deposition parameters and film structure is still lacking (see refs. 1–3). In reality even small changes in the process parameters can cause significant changes in the composition and structure of films. This has led to wide differences in the properties of TiN films produced in different laboratories by various methods.

In this paper we present the results of compositional analysis of titanium nitride films, obtained by different techniques in the laboratories of Salford University and in several laboratories in Moscow.

The following methods were used for the preparation of the thin TiN films: (i) low energy ion-assisted deposition (IAD) under various conditions—Salford; (ii) deposition in a cathode spot arc discharge system (CSAD)—Moscow; (iii) deposition in a planar magnetron (PM)—Moscow.

The films were deposited on to steel, hard alloy, or

silicon substrates and then analysed by X-ray photoelectron spectroscopy (XPS) (Moscow). The choice of different substrates was made to allow hardness and tribological measurements to be performed and these will be reported in a future publication.

It was of interest to analyse not only the composition of films, but also to determine the states of chemical bonding between the film components (primarily to confirm the presence of compounds such as TiN). XPS is the most suitable for this task [4–15] and it is for this reason that this method has been used for most of the analysis. Rutherford backscattering spectrometry (RBS) was also used immediately after preparation of IAD films.

2. Experimental details

The three different methods listed above were used to produce the titanium nitride films and these are now described.

2.1. Low energy ion assisted deposition (IAD)

Two Kaufman sources were used, one mounted vertically to provide a sputtering ion beam, the other mounted horizontally to provide the energy assisting ion beam. The Kaufman source for sputtering was a three-grid type and delivered a beam of 1 keV Ar⁺ ions

of intensity $250\text{--}350\text{ }\mu\text{A cm}^{-2}$, depending on source parameters. The Kaufman source for ion-assisted deposition is a two-grid source which is operated in the range $100\text{--}500\text{ eV}$ for this work. It can deliver Ar^+ or N_2^+ ions with current densities in the range $5\text{--}50\text{ }\mu\text{A cm}^{-2}$ depending on energy and source parameters. Chamber pressure is measured by an ionization gauge and there is a mass spectrometer to monitor background gases. Base pressures in the chamber are better than $5 \times 10^{-7}\text{ mbar}$ but rise to $3 \times 10^{-4}\text{ mbar}$ during deposition.

Films were deposited onto 1 cm^2 (100) silicon wafers which were etched in HF and rinsed in deionized water immediately prior to insertion into the vacuum chamber. After chemical cleaning the substrates were etched by 400 eV Ar^+ ions ($40\text{ }\mu\text{A cm}^{-2}$ for 20 min) to remove any remaining oxide layer before deposition. The titanium target was also sputter-cleaned using a 1 keV Ar^+ beam ($350\text{ }\mu\text{A cm}^{-2}$ for 10 min) before the commencement of the experiment.

Three different types of experiment were performed.

(a) Reactive sputtering, *i.e.* sputter deposition under different partial pressures of nitrogen without ion bombardment during the film growth. In these experiments deposition was carried out using 1 keV Ar^+ ion bombardment of Ti with a current density $250\text{ }\mu\text{A cm}^{-2}$.

(b) Deposition concurrent with Ar^+ ion bombardment of the film during its growth under various partial pressures of nitrogen.

(c) Deposition concurrent with N_2^+ ion bombardment of the film during its growth under various partial pressures of nitrogen.

For reactive sputtering in a nitrogen pressure of $p_{\text{N}} > 5 \times 10^{-5}\text{ mbar}$, the TiN films were gold-like in appearance. Films obtained in this regime will be referred to later as samples 1. When Ar^+ ion assistance was used the films were copper-coloured (referred to as samples 2) or silver-coloured (samples 3). The irradiation of the substrate by nitrogen ions during titanium target sputtering (case (c)) produced blue-coloured films (samples 4).

2.2. Deposition in the cathode spot arc discharge system (CSAD)

After ultrasonic cleaning in a freon bath and drying in freon vapour, the samples of hard alloy (WC 79%, TiC 15%, Co 6%) or steel were inserted into the sample holder in the vacuum chamber. Two stages of cleaning *in situ* were performed with each sample:

(i) *Cleaning in a glow discharge.* After reaching a base pressure of approx. $2 \times 10^{-5}\text{ mbar}$, nitrogen of high purity was admitted up to approx. 10^{-2} mbar into the sample chamber. A negative voltage of -1.5 kV was applied to the sample holder with respect to the walls of the chamber, and a glow discharge was struck between

the holder (cathode) and the walls of the chamber (anode). The duration of cleaning in the glow discharge was 15 min with a current density $j = 0.5\text{ mA cm}^{-2}$.

(ii) *Cleaning by titanium ion sputtering.* The nitrogen flow was turned off and the chamber was again pumped down to approx. $2 \times 10^{-5}\text{ mbar}$. Titanium ions were produced in the cathode spot arc source by electron impact ionization of titanium vapour. The negative bias on the sample was -1.5 kV and the arc discharge current in the source was 70 A. The density of titanium ion flux n near the surface of the rotating substrate (2 rotations per minute) was 10^{11} cm^{-3} and the duration of Ti ion bombardment of the sample surface was 300 s. The temperature of the sample surface towards the end of ion bombardment was 650°C .

The investigations of the cleaning process showed that it is accompanied by the formation of an intermediate layer of titanium. The measured intensities of the Ti $K\alpha$ line emission from the surface show that, in only 3–5 s, a 15–30 nm thick titanium layer forms on the surface of the steel specimen. An increase in the time of Ti ion bombardment up to 10 s leads to a linear increase in the Ti layer thickness. Further increase in the sputter cleaning time up to 30 s leads to a slight decrease in the titanium deposition rate. After 300 s, the effective Ti layer thickness is as great as 300 nm. The presence of this thin titanium layer after cleaning by Ti ion bombardment leads to good adhesion between the substrate and the coating.

After cleaning, nitrogen was again admitted into the sample chamber (up to $p = 10^{-3}\text{ mbar}$), the substrate bias was brought up to -200 V , and the arc source was run. Coating deposition was performed by two ion sources working simultaneously under equal conditions (arc discharge current $I = 70\text{ A}$). The film deposition time was 30 min and the speed of rotation of the sample was 2 rev min^{-1} . TiN coatings formed were about $5\text{ }\mu\text{m}$ thick. Films obtained by this CSAD method will be referred to as samples 5.

2.3. Deposition in a planar magnetron

A conventional diode magnetron sputtering system ("Mir-2") was used. The substrates, of stainless steel, were ultrasonically cleaned in a freon bath and dried in freon vapour, as for the CSAD films described previously. They were then cleaned by ion bombardment and heating as follows:

(a) in $5\text{--}7 \times 10^{-2}\text{ mbar}$ argon glow discharge at 1500 V substrate potential and 0.7–1 A discharge current for 20 min (a time when sparking on the substrate surface stopped and the discharge current increased)

(b) heated to 670°C in a reduced pressure of $5 \times 10^{-5}\text{ mbar}$ (argon plus residual gas)

(c) repetition of (a) and (b) but with the heating continued for 90 min.

Magnetron sputtering took place at a working pressure of approx. 3×10^{-2} mbar, the working gas being argon or nitrogen. The discharge voltage was 560 V and the current 6 A. Sputter targets were made from compressed TiN powder and a negative bias was applied to the substrates. Films of 7–10 μm thickness were formed in 30 min. These samples will be referred to as samples 6.

3. X-ray photoelectron spectroscopy analysis of film composition

3.1. Analysis procedure

3.1.1. Experimental details

Measurements were performed on a Kratos XSAM800 XPS/Auger electron spectroscopy (AES) spectrometer equipped with a single channel hemispherical analyser, quadrupole anode X-ray gun and duoplasmatron ion gun.

To determine the chemical states of oxygen, nitrogen, carbon and titanium the spectra of the O 1s, N 1s, O 1s and Ti 2p lines, usually used for these elements, were recorded. The samples were excited with Al K α (1486.6 eV) radiation for survey spectra and with Mg K α (1253.6 eV) for the C 1s, Ti 2p, N 1s and O 1s peaks. Survey spectra were collected at a pass energy of 65 eV (1 eV per step). High resolution spectra were obtained at a pass energy of 38 eV (0.2 eV per step). All the data were obtained in a fixed analyser transmission mode, giving a full width at half-maximum (FWHM) value of 1.3 eV for the Ag 3d_{5/2} line. The analyser lens was in the high magnification mode with an analysis area of $1.5 \times 2.5 \text{ mm}^2$. Ion bombardment in all cases was performed with 6 keV Ar⁺ ions at an incidence angle of 45°, raster scanned over an area of $7 \times 7 \text{ mm}^2$, so that sputtering was uniform in the area of analysis. The ion current was in the 2.5–3.0 μA range and the base pressure was below 5×10^{-9} mbar. The binding energy (BE) reference for XPS was the Ag 3d core line (BE = 367.9 eV). Calibration of the spectra was based upon the C 1s peak (BE = 285 eV) owing to residual hydrocarbon. The intensity ratios of the Ti 2p, N 1s, O 1s and C 1s peaks were determined from peak areas obtained by integration of the peaks after smoothing and background subtraction (Shirley method [13]). Atomic concentration calculations were made using the atomic sensitivity factors provided by the manufacturer of the instrument. Normally the near-surface region of Ti films contains not only TiN compounds, but also oxides and oxynitrides. The content of the nitride state appears to be dependent on the method and conditions of the deposition of the coating. The published data on the Ti 2p spectra of the initial surface show peaks corre-

sponding to the TiN and TiO states. The contribution of different Ti chemical states to the spectra is usually found by using a curve-fitting procedure, combined with various background subtraction methods, with a gaussian–lorentzian peak shape used for the major components [5–7,14]. The separation of the exact TiN spectrum from experimental spectra of the films is rather complicated [15] owing to such factors as Coster–Kronig broadening, intense satellites and discrete energy losses, which are usually attributed to the oxynitride state and to the uncertainty in the binding energy position of the oxynitride state. This may cause errors in determination of the titanium nitride state content in the coating. In this work we attempted to minimize errors by using experimental reference spectra of TiN and TiO₂.

We note that, in the nitrogen N 1s spectrum, two lines usually attributed to the presence of stoichiometric and nonstoichiometric titanium nitride TiN and TiN_x with $x > 1$ are observed [6]. We will also use this interpretation, but we think that there is another possible explanation. In the Ti 2p spectrum only the line corresponding to stoichiometric TiN is observed, while the line corresponding to nonstoichiometric TiN_x is not present. This implies that, although the nitrogen content in the film is somewhat larger than in pure TiN, all the Ti atoms are in the chemical state corresponding to stoichiometric TiN. At the same time the presence of two lines of titanium nitride in the N 1s spectrum shows that there are two types of nitrogen chemical states, one with all the bonds characteristic of pure TiN, the other having some unsaturated bonds.

3.1.2. Curve fitting procedure for the spectra

From previous XPS core level measurements of pure TiO₂ (anatase) and TiN we have obtained the reference spectra of TiO₂ and TiN. The latter has the same shape as the spectrum of TiN single crystal [4]. These spectra are used as the starting conditions to fit the experimental data. Unfortunately, we did not have standard Ti 2p lines for oxynitrides, and no published data on the spectra of these compounds are available to us. In principle, the standard approach could be used, when the spectra are presented in the form of gaussian–lorentzian peaks, but we have chosen the following procedure: the oxynitride line shapes were obtained as the superposition of the TiN and TiO₂ spectra with different relative intensities, thus providing a wide range of oxynitride states with FWHM between 2.2 eV (TiO₂) and 2.8 eV (TiN). We believe that this approach allowed us to account to some extent for the contribution to the Ti 2p line of discrete losses, which come into play during interaction of Ti and N [15]. This procedure is somewhat arbitrary, but in fact it is no more arbitrary than using smooth curves to describe complex XPS spectra.

Note that the state with larger FWHM has a larger binding energy. As will be shown below, the curve-fitting procedure did not always preserve the difference between the binding energies of the TiO_2 and TiN states when the Ti 2p spectrum was analysed. At the same time, the difference between the binding energies of the O 1s and Ti 2p line components attributed to TiO_2 ($\Delta = E_{\text{Ti } 2p} - E_{\text{O } 1s} = 72 \text{ eV}$) [5] is equal for all the samples. These lines are shifted simultaneously with respect to other lines (N 1s, O 1s, and Ti 2p for TiN). This fact may be related to the presence of nonconductive islands of TiO_2 in the near-surface region. In this case these lines can be shifted as a result of surface charging, but the distance between them should remain constant. The shift value should depend on the size of the islands and on the dielectric constant within the matrix, and may be different for different samples.

When fitting the N 1s line, the difference between the energy positions $\Delta = E_{\text{Ti } 2p} - E_{\text{N } 1s}$ was calculated from the TiN reference spectrum. This difference is equal to 58 eV and has an intermediate position between similar data found in ref. 5 (57.8 eV) and in ref. 6 (58.4 eV). We relate the line with binding energy of 1 eV lower than TiN to the energy of the state corresponding to nonstoichiometric TiN_x ($1 < x < 1.5$) in accordance with ref. 7.

The titanium nitride chemical state lines were described by gaussian peak shapes with $\text{FWHM} = 1.6 \text{ eV}$; a FWHM within the range 1.8–2.0 eV was chosen for the oxynitride states. The high-energy part of the spectrum was described using two states corresponding to oxynitrides [7]. However, in several cases (samples 4–6), one more nitrogen state with the largest energy had to be introduced to describe the spectra adequately. The nature of this state is to be studied in future.

It should be noted that we have taken two oxynitride states, as has been done in other work (e.g. ref. 6), but we do not know how many oxynitride states are really present. Probably it would have been more correct to take the total area under each curve as a measure of the oxynitride state content with no distinction between these states.

3.2. Composition of the initial film surface

3.2.1. Ti 2p spectra

The shapes of the photoelectron spectra of Ti 2p lines for the samples studied (Fig. 1) are significantly different. The analysis shows that characteristic peaks of the titanium nitride state are present for samples 1, 5 and 6. Note that a lower content of the titanium nitride state corresponds to a lower slope of the low-energy part of the spectrum in Fig. 1. The state corresponding to TiO_2 is also clearly present for all the films. The result of the curve-fitting procedure for the Ti 2p spectrum for sample 1 is presented in Fig. 2. The Ti 2p spectrum is the sum of three components: $\text{TiN} + \text{TiN}_x$ ($x > 1$), line 1

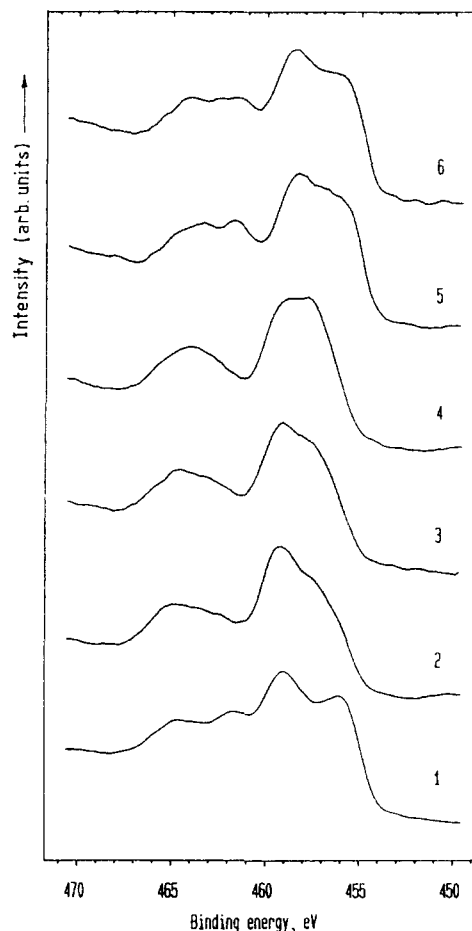


Fig. 1. XPS spectra of the Ti 2p state from samples 1–6 as received.

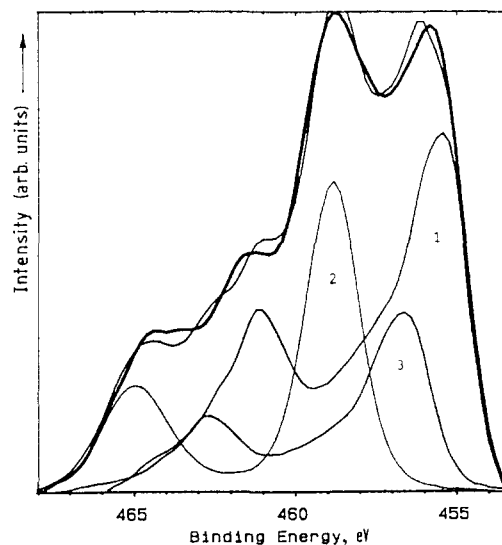


Fig. 2. Ti 2p experimental core-level spectra (—) and the result of fitting (---) for sample 1 using the components 1. TiN ; 2. TiO_2 ; 3. TiN_xO_z ($y > z$).

(BE=455.2 eV); TiO_2 , line 2 (BE=458.6 eV); TiN_yO_z ($y > z$), line 3 (BE=456.4 eV). These results are in conformity with other data in the literature [3].

3.2.2. N 1s spectra

The N 1s spectra for the six samples are different in the low-energy region and in the widths (FWHM) of the central parts of the spectra. This is an indication of the presence of different amounts of oxynitride states. This effect is most pronounced for the samples 5 and 6 which have a large FWHM. From the widths and shapes of the N 1s photoelectron lines, as well as from the results of the curve-fitting procedure for the Ti 2p lines, it follows that several nitrogen states are present in the initial surfaces. Figure 3 shows some nitrogen states for samples 1. The binding energy of these states are as follows: 397.2 eV, TiN (line 1); 396.3 eV, nonstoichiometric TiN_x (line 2); 398.8 eV, TiN_yO_z (line 3); 400.6 eV, TiN_uO_v (line 4). The oxynitride state with smaller binding energy is characterized by smaller oxygen concentration and larger nitrogen concentration; in the figures and tables it is denoted as TiN_yO_z ($y > z$). The compound TiN_uO_v ($u < v$) corresponds to an oxynitride with larger oxygen concentration and smaller nitrogen concentration, i.e. we suppose that $u < y$ and $v > z$. The TiN_yO_z oxynitride is characterized by a FWHM of 2.6 eV, and the FWHM for TiN_uO_v is 2.4 eV.

3.2.3. O 1s spectra

The analysis of oxygen O 1s photoelectron spectra demonstrates that not less than three states are needed to describe the oxygen states on the surface. There are two states representing oxygen in the oxynitride: TiN_uO_v ,

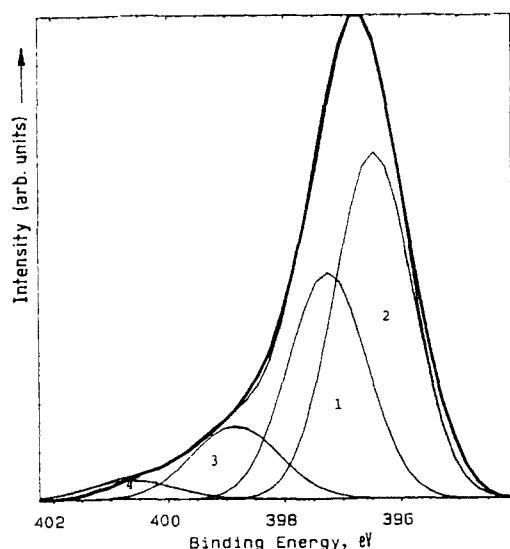


Fig. 3. N 1s experimental core-level spectra (—) and the result of fitting (—) for sample 1 as received using the components 1, TiN; 2, nonstoichiometric TiN_x ($x > 1$); 3, TiN_yO_z ($y > z$); 4, TiN_uO_v ($u < v$).

($u < v$) (BE=533.5 eV) and TiN_yO_z ($y > z$) (BE=532.0 eV), and a third state representing oxygen in the TiO_2 chemical state (BE=530.5 eV). From the O 1s spectra it can be seen that the content of different oxygen states varies for different samples.

3.2.4. Comparison of the initial surface chemical composition of different coatings

As shown in the discussion above, the curve-fitting procedure for the Ti 2p line allows the determination of the relative intensities of the TiN + TiN_x and oxynitride states of titanium. However, the determination of the stoichiometric TiN contribution alone to the nitride state is impossible, since the Ti 2p line is insensitive to the change in x [6]. However the N 1s line is sensitive to changes in x and the results of the curve-fitting procedure of the N 1s line allow us to determine the relative contribution of stoichiometric TiN. The results of the analysis of the chemical composition of the samples are given in Table 1. It is seen from Table 1 that, near the film-substrate interface, the TiN content is greatest for the golden-coloured samples (1, 5 and 6). The TiN content is lower and the TiO_2 and TiN_yO_z contents are higher for dark-coloured samples (2, 3 and 4). It is of interest to note that, in addition to stoichiometric TiN, a significant content of nitrogen-enriched titanium nitride (TiN_x with $x > 1$) is present. This result correlates with the work of Krusin-Elbaum *et al.* [16], where zirconium nitride (which is similar to TiN in its chemical properties) films were found to contain a ZrN_x ($2/3 < x < 3/2$) compound.

The percentage of stoichiometric titanium nitride in the steady state is largest for samples 1 and 6 (reactively and magnetron sputtered films respectively). As a general rule the golden-coloured samples have larger content of stoichiometric titanium nitride, i.e. there is a correlation between relative TiN concentration and the colour.

One should note that the percentage of TiO_2 for different samples does not change very much (from 25% to 34%); this could be explained by the fact that the creation of TiO_2 is connected not with the film deposition process itself, but with the vacuum conditions and sample history after this process is completed. Indeed RBS measurements, taken within a few days of deposition, showed that the oxygen content of samples 1–4 was less than 1%. The results obtained for both the Ti 2p and N 1s spectra suggest that the final sample coatings have a surface with a significant amount of TiO_2 and an intermediate oxynitride phase. The content of TiO_2 in titanium nitride films has also been monitored by other groups [5–7,14] who showed that presence of this compound does not necessarily mean that the engineering performance of the film is not good.

TABLE 1. Compound composition in films (%)

Compounds in films ^a		Reference number of film, colour and method of preparation					
		1 Golden IB (reactive)	2 Silver-like IAD (Ar)	3 Copper-like IAD (Ar)	4 Blue IAD (N)	5 Golden IP	6 Golden PM
TiN	1	19	8	6	7	5	39
	2	57	36	36	41	43	63
TiN _x (1 < x < 1.5)	1	30	10	4	5	42	11
	2	18	23	27	17	18	33
TiN _y O _z (y > z)	1	22	36	42	39	19	24
	2	12	17	20	21	21	4
TiN _u O _v (u < v)	1	-	12	20	24	9	-
	2	8	16	-	15	-	-
TiO ₂	1	29	34	28	25	25	26
	2	-	-	-	-	-	-
TiO	1	-	-	-	-	-	-
	2	5	8	17	13	18	-

^a 1. As received; 2. after ion etching to a depth of 300 Å.

3.3. Composition of the films after ion etching (depth analysis)

Ion-beam etching completely removes TiO₂, reduces the content of the oxynitrides, and raises the content of TiN at the surface (see Table 1). However, it seems impossible to trace the chemical content at the surface during the etching process in terms of the above-mentioned states. This is due to the fact that ion bombardment causes breaking of chemical bonds and formation of new chemical states. Specifically, the breaking of the Ti-O and Ti-N bonds with subsequent recombination may lead to an oxynitride state formation. Thus the description of the decomposition of TiO₂ could require as many as five chemical states. To our knowledge, there are no available results concerning the effect of ion bombardment on the chemical state of oxynitrides. Long-term etching allows the removal of the destroyed layer and an evaluation of the chemical composition of the coating in depth. Fortunately preferential sputtering effects in TiN are negligible [8-10]. Thus, ion etching may allow determination of the Ti chemical state in the bulk to an accuracy which depends on the uncertainty in the preferential sputtering effects in titanium oxynitride and on the content of the oxynitride state.

3.3.1. Ti 2p spectra

The analysis of the Ti 2p lines (Fig. 4), recorded after removal of the upper 300-500 Å of the films, showed that in all cases the content of TiN is larger in the bulk than at the surface. TiO₂ has almost completely disap-

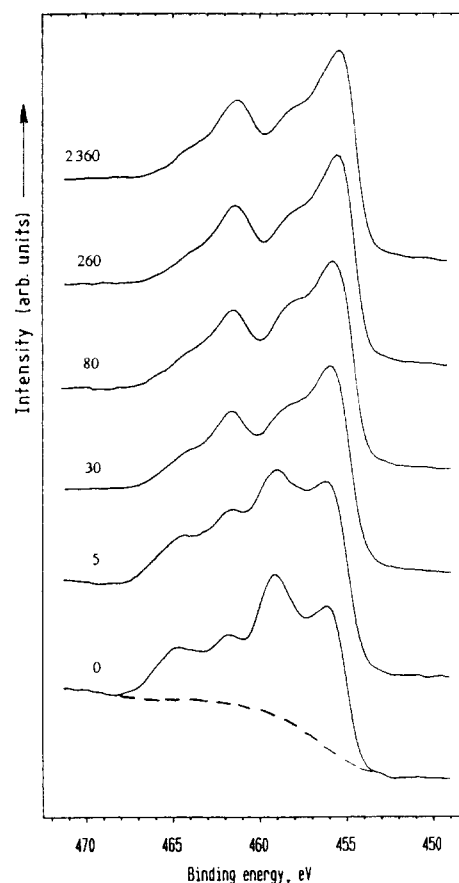


Fig. 4. Change in XPS spectra of the Ti 2p line during ion etching of sample 1. Etching depth in ångströms is shown above each curve. The dashed line represents the background.

peared but in all the samples (except for 6) a TiO compound appeared. A comparison of the spectra presented in Figs. 2 and 4 clearly shows a decrease in the content of TiN_yO_z and a reduction in TiO_2 . Figures 4 and 5 present the data on the contributions of various Ti and N states for the samples 1, 4, 5 and 6, and Table 2 lists the data on the chemical composition of the samples.

These data suggest that the removal of such a thick layer was not accompanied by complete removal of the oxynitride state. From a comparison of the measurements made before and after etching it follows that samples with larger content of oxygen in the bulk have a larger degree of surface oxidation. Since the steady-state spectra were recorded after the removal of approx.

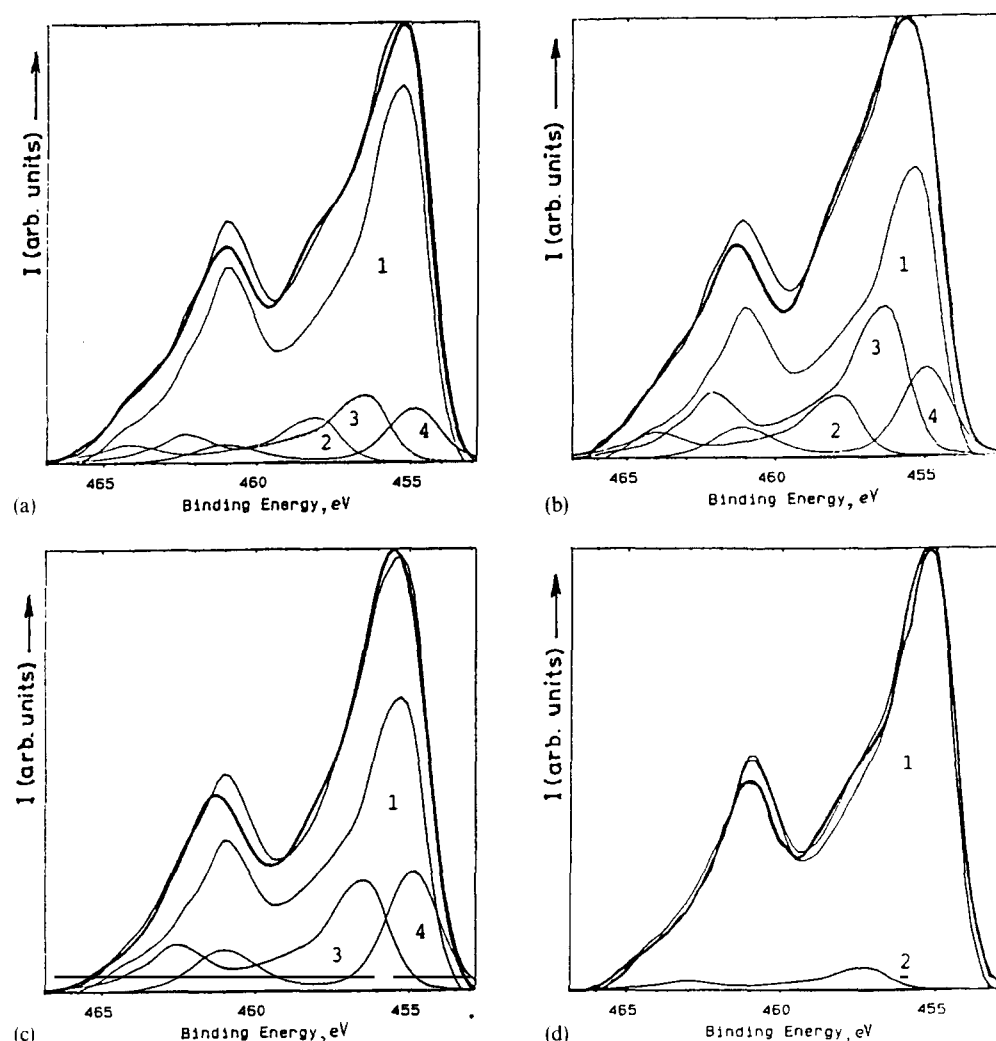


Fig. 5. Ti 2p experimental core-level spectra (—) and the result of fitting (---) for samples 1, (a); 4, (b); 5, (c); 6, (d) in steady state conditions after the removal of a 300 Å layer by ion etching, using the components 1, TiN; 2, TiN_yO_z ($y > z$); 3, TiN_uO_v ($u < v$); 4, TiO.

TABLE 2. Depth composition of films

Sample number	Removed thickness (Å)						
	0 (surface)	5	30	80	160	260	360
1	$\text{TiN}_{1.1}\text{O}_1\text{C}_{0.2}$	$\text{TiN}_1\text{O}_1\text{C}_{0.09}$	$\text{TiN}_{1.1}\text{O}_{0.6}\text{C}_{0.04}$	$\text{TiN}_{1.2}\text{O}_{0.5}\text{C}_{0.02}$	$\text{TiN}_{1.2}\text{O}_{0.4}$	$\text{TiN}_{1.2}\text{O}_{0.4}$	$\text{TiN}_{1.2}\text{O}_{0.4}$
2	$\text{TiN}_{1.3}\text{O}_{1.6}\text{C}_{1.3}$	$\text{TiN}_{1.2}\text{O}_{1.1}\text{C}_{0.2}$	$\text{TiN}_{1.4}\text{O}_{0.7}$	$\text{TiN}_{1.4}\text{O}_{0.6}$	$\text{TiN}_{1.4}\text{O}_{0.3}$	$\text{TiN}_{1.3}\text{O}_{0.5}$	$\text{TiN}_{1.3}\text{O}_{0.5}$
3	$\text{TiN}_{1.2}\text{O}_{1.7}\text{C}_{1.4}$	$\text{TiN}_{1.2}\text{O}_{1.2}\text{C}_{0.5}$	$\text{TiN}_{1.4}\text{O}_{0.6}\text{C}_{0.03}$	$\text{TiN}_{1.3}\text{O}_{0.4}$	$\text{TiN}_{1.3}\text{O}_{0.4}$	$\text{TiN}_{1.3}\text{O}_{0.4}$	$\text{TiN}_{1.3}\text{O}_{0.4}$
4	$\text{TiN}_{1.3}\text{O}_{1.9}\text{C}_{3.7}$	$\text{TiN}_{1.3}\text{O}_{1.1}\text{C}_{0.8}$	$\text{TiN}_{1.3}\text{O}_{0.7}\text{C}_{0.2}$	$\text{TiN}_{1.3}\text{O}_{0.9}\text{C}_{0.4}$	$\text{TiN}_{1.2}\text{O}_{0.9}\text{C}_{0.3}$	$\text{TiN}_{1.2}\text{O}_{0.9}\text{C}_{0.3}$	$\text{TiN}_{1.4}\text{O}_{0.4}\text{C}_{0.4}$
5	$\text{TiN}_{1.4}\text{O}_{1.3}\text{C}_{4.8}$	$\text{TiN}_{1.2}\text{O}_{0.4}\text{C}_{1.4}$	$\text{TiN}_{1.2}\text{O}_{0.2}\text{C}_{0.5}$	$\text{TiN}_{1.2}\text{O}_{0.2}\text{C}_{0.4}$	$\text{TiN}_{1.2}\text{O}_{0.9}\text{C}_{0.3}$	$\text{TiN}_{1.2}\text{O}_{0.1}\text{C}_{0.2}$	$\text{TiN}_{1.2}\text{O}_{0.1}\text{C}_{0.2}$
6	$\text{TiN}_1\text{O}_{0.9}\text{C}_{3.6}$	$\text{TiN}_1\text{O}_{0.6}\text{C}_{0.8}$	$\text{TiN}_{0.9}\text{O}_{0.5}\text{C}_{0.4}$	$\text{TiN}_{0.2}\text{O}_{0.3}\text{C}_{0.03}$	$\text{TiN}_{0.9}\text{O}_{0.3}\text{C}_{0.03}$	$\text{TiN}_{0.9}\text{O}_{0.3}$	$\text{TiN}_{0.9}\text{O}_{0.3}$

300–500 Å of the coating, the presence of oxygen in the bulk is unlikely to be a consequence of recoil implantation of oxygen atoms from the near-surface layer. This effect is more likely to be related to the features of the particular coating deposition method. It is probable that the film during growth is porous and is strongly reactive to ambient gases.

3.3.2. N 1s spectra

The analysis of the N 1s spectra shows that, as for the Ti 2p spectra, ion bombardment leads to a redistribution of the relative contents of different states. From the data it appears that the relative content of stoichiometric TiN increases, and the content of nonstoichiometric TiN is reduced. This trend holds for all the samples.

3.3.3. O 1s spectra

During the evolution towards the steady-state the shape of the O 1s spectrum was seen to change. This effect is attributed to the removal of chemisorbed oxygen and of TiO₂. The recorded spectra can be described using two oxynitride states (Fig. 6).

4. Conclusions

The results of the XPS analysis of the composition of titanium nitride films obtained by various methods: ion-assisted deposition (IAD), ion plating (IP) and planar magnetron sputtering (PM) may be presented as follows.

(1) Titanium nitride films of different colour, obtained using various regimes of deposition, have markedly different composition. The dark-coloured films (blue,

copper-like and silver-like) are characterized by the presence of a significant quantity of oxynitrides and titanium oxides, both at the surface and in the bulk. Thus the blue-coloured film obtained by ion-assisted deposition contains only 10% titanium nitride at the surface and about 60% in the bulk, the rest being oxynitrides and oxides; the concentrations of oxynitrides and oxides are twice as large at the surface than in the bulk (these concentrations are 60% and 25% at the surface and 35% and 10% in the bulk respectively). As RBS measurements taken just after deposition of these films showed that the oxygen content was very low it is possible that their composition has changed with exposure to air.

(2) All the films under investigation (of any colour) contain a fraction of titanium nitride enriched with nitrogen (TiN_x, $x > 1$) in addition to stoichiometric titanium nitride TiN.

(3) The content of titanium nitride TiN + TiN_x in the golden-coloured films obtained by all the three methods is the same (approximately 50% at the surface). The content of stoichiometric titanium nitride TiN is largest for the film obtained by using the PM method.

(4) Bulk content of titanium nitride TiN + TiN_x is approx. 75% and 95% for golden-coloured films obtained using ion-assisted and planar magnetron methods respectively. In both these cases the content of the stoichiometric titanium nitride in the bulk is about 60%.

Acknowledgment

The authors are grateful to the British Council and to the Russian State Committee of Higher Education for the support of this investigation. We also wish to thank O. Ivanova and A. Promokhov for the assistance in making the measurements and in the preparation of the manuscript.

References

- 1 J. M. E. Harper, J. E. Cuomo, R. J. Gambino and H. R. Kaufman, in O. Auciello and R. Kelly (eds.), *Ion Bombardment Modification of Surfaces* Elsevier, Amsterdam, 1984, Chapter 6, p. 127.
- 2 J. E. Greene, S. A. Barnett, J. E. Sundgren and A. Rockett, in T. Itoh (ed.), *Ion Assisted Film Growth*, Elsevier, Amsterdam, 1989, Chapter 5, p. 101.
- 3 H. Kheyandish, J. K. Kim and J. S. Colligon, *J. Vac. Sci. Technol.*, 1994 (submitted for publication).
- 4 A. J. Perry, C. Strandberg, W. D. Sproul, S. Hofmann, C. Ernsberger, J. Nickerson and L. Chollet, *Thin Solid Films*, 153 (1987) 169.
- 5 A. R. Nyaiesh, E. L. Garwin, F. K. King and R. E. Kirby, *J. Vac. Sci. Technol.*, A4 (1986) 2356.
- 6 K. S. Robinson and P. M. A. Sherwood, *Surf. Interface Anal.*, 6 (1984) 261.

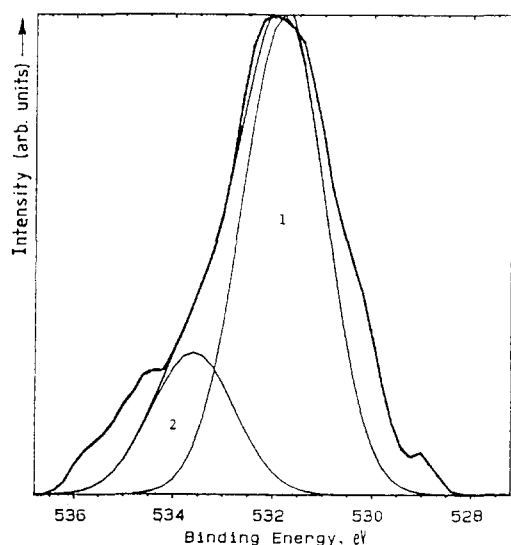


Fig. 6. O 1s experimental core-level spectra (—) and the result of fitting (---) for sample 1 after ion etching to a depth of approx. 300 Å, using the components 1, TiN_yO_z ($y > z$); 2, TiN_uO_v ($u < v$).

- 7 B. J. Tan, L. Hwan, S. L. Suib and F. S. Galasso, *J. Vac. Sci. Technol.*, *A9* (1991) 2196.
- 8 S. Hofmann, *J. Vac. Sci. Technol.*, *A4* (1986) 2789.
- 9 P. T. Dawson and K. K. Tzatzov, *Surf. Sci.*, *149* (1985) 105.
- 10 N. Kaufherr and D. Lichtman, *J. Vac. Sci. Technol.*, *A3* (1983) 1969.
- 11 A. Ermolief, P. Bernard, S. Marthon and P. Wittmar, *Surf. Interface Anal.*, *11* (1988) 563.
- 12 H. Bender, J. Portillo and W. Vandervorst, *Surf. Interface Anal.*, *14* (1989) 337.
- 13 P. Saillard, A. Gicquel, J. Amouroux, N. Moncoffre and J. Tousset, *Surf. Interface Anal.*, *16* (1990) 530.
- 14 J. Halbritter, H. Leiste, H. J. Mathes and P. Walk, *Fresenius J. Anal. Chem.*, *341* (1991) 320.
- 15 I. leR. Strydom and S. Hofmann, *J. Electron Spectrosc. Relat. Phenom.*, *56* (1991) 85.
- 16 L. Krunsin-Elbaum, M. Winter, C.-Y. Ting and J. J. Cuomo, *Thin Solid Films*, *104* (1983) 81.