FORMATION AND CHARACTERIZATION OF TITANIUM NITRIDE AND TITANIUM CARBIDE FILMS PREPARED BY REACTIVE SPUTTERING

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ABSTRACT
Titanium has been reactively r.f. sputtered in mixed Ar-N₂ and Ar-CH₄ discharges on to substrates held at 775 K. The films obtained have been characterized by scanning electron microscopy, X-ray diffraction and by measurements of hardness and electrical resistivity. The compositions of the films have been determined using Auger electron spectroscopy. The processes occurring both on substrates and target surfaces have been studied and it is shown that the latter is of great importance for the composition and structure of deposited films.

Titanium nitride films of full density and with electrical resistivity and hardness values close to those of bulk TiN were only obtained in a narrow range close to the stoichiometric composition. Titanium carbide films grown on non-biased substrates were found to have an open structure and thus a low density. A bias applied to the substrate, however, improved the quality of the films.

It is also shown that the heat of formation of the compounds plays an important role in the formation of carbides and nitrides. A large value promotes the development of large grains and dense structures.

INDEX TERMS
Titanium nitride, titanium carbide, reactive sputtering, thin films, structure, composition, hardness, electrical resistivity, target reactions, substrate bias, Auger analysis.

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Linköping 1982
Life is what happens to you
While you're busy
Making other plans

From Beautiful boy (Darling boy)
by John Lennon
This thesis is based on work carried out at the Department of Physics and Measurement technology, Linköping University, during the period 1979-82. The work has been performed in collaboration with Bengt-Olof Johansson and also in some part with Hans Hentzell.

The thesis consists of seven chapters which even if they can be read separately are inter-connected and depend on each other.

Chapter I is an introduction which is written to give a background and introduce even the nonspecialist into the field.

Chapter II describes the experimental equipment and the methods of film analysis used.

Chapter III to VII consist of the following articles:


Mechanisms of reactive sputtering of titanium nitride and titanium carbide.

II Morphology and Structure.
Submitted to Thin Solid Films.

III Influence of substrate bias on composition and structure.
Submitted to Thin Solid Films.
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The patient assistance of Siv Söderlund in preparing the manuscript, of Paul Krantz in making the drawings, of Hans Edeson and Leif Johnson in making copies of all the figures, and of Peter Dougan for correcting my English is also greatly appreciated.

Without the support and solidarity of my wife, Inger, I guess that the following pages should not have existed yet.

Ujebro march 1982

Jan-Eric Sundgren
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THIN FILMS OF CARBIDES AND NITRIDES

WHY AND HOW?

1. INTRODUCTION

Why is there an interest in thin films of carbides and nitrides? How are these films prepared? What do the films look like? How is their adhesion? These questions are usually asked, and while in this paper we will answer some of them, for others no general answer can be given. In the first two sections the question Why? is answered and in section 3 questions concerning How? and What? are discussed.

2. WHY?

The current interest in transition-metal carbides and nitrides is due to the many unique properties that these compounds exhibit. Most of them have extremely high melting points (2000-4000°C) why they frequently are referred to as "refractory carbides and nitrides". However, their main commercial importance results from their high hardness. For example "cemented carbide" or hard metals which are frequently used as cutting-tools and wear-resistant parts are composite materials consisting of carbide grains, mainly tungsten carbide (WC) but TiC, NbC and TaC can also be used, surrounded by a binder phase usually of cobalt. Carbides and nitrides are also finding new areas of application due to their electrical and superconducting properties. An excellent review of this area is given in the book "Transition metal carbides and nitrides" by L.E. Toth [1] and the reader is warmly recommended to consult it for detailed descriptions and discussions of their different properties. Here only a brief description of their most unusual properties and most common areas of application is given. Much of the information presented here originates from the book mentioned above.
2.1 Properties

Hardness. The transition metal carbides and nitrides are among the hardest compounds known. Most of them have hardness values between 2000 and 3000 kp mm\(^{-2}\). The carbides are generally somewhat harder than the nitrides. At room temperature, TiC is the hardest carbide (~3000 kp mm\(^{-2}\)) but it rapidly loses its hardness at elevated temperatures, e.g., at 600\(^0\)C the hardness is reduced to 1000 kp mm\(^{-2}\). WC is the hardest carbide at elevated temperatures, its hardness is ~1800 kpmm\(^{-2}\) at 600\(^0\)C. Hafnium nitride, HfN, is also a material with a low decrease in hardness with increasing temperature.

Melting temperature. As already mentioned, the melting or decomposition temperatures of these compounds are extremely high, around 3000\(^0\)C. Tantalum carbide, TaC, as the extreme melts at 3983\(^0\)C.

Structure. These compounds have generally a broad range of compositions in which they are stable and thus appreciable vacancy concentrations, up to 50 at.\%, can exist on the non-metal sites. The presence of such large concentrations of vacancies affects many of their electrical, mechanical and superconducting properties. In Figs. 1 and 2, equilibrium phase diagrams are shown for Ti-C and Ti-N respectively.

Strength. Specially the carbides are extremely strong particulary at high temperatures. They have e.g., values of Young's modulus that are about a factor-of-two higher than that of most transition-metals. At room temperature they are brittle, but at temperatures above ~1000\(^0\)C they undergo a brittle-to-ductile transition.

Chemical reactivity. They are chemically stable at room temperature and are attacked only slowly by strong acid solutions.
Fig. 1 Phase diagram for titanium-carbon (from L.E. Toth [1]).

Fig. 2. Phase diagram for titanium-nitrogen (from L.E. Toth [1]).
**Electrical properties.** They are typically metallic in their electrical properties. The electrical conductivity of, e.g., stoichiometric TiN is almost a factor of two higher than that of pure titanium. Due to the large vacancy concentration in the carbides and nitrides the temperature dependence of the electrical resistivity is small.

**Superconducting properties.** Nitrides form an interesting class of superconductors, e.g., NbN-based alloys have superconducting critical temperatures as high as 18 K.

2.2 **Applications**

As already mentioned, the largest area of application is as the main constituent in cemented carbide cutting tools. In the middle of the 1960s the wear resistance of such tools was increased appreciably by the deposition of thin coatings of TiC, TiN and other refractory compounds [2, 3]. The increase in the lifetimes of the tools due to such coatings depends on both the improved wear resistance and the lower cutting temperature due to a reduced friction between the work material and the tool. The area of application for these types of coatings has been extended during the last years to, e.g., tools of ordinary tool-steels and high-speed steels. Commercially, for instance high speed steel drills coated with TiN [4] have been introduced. The wear life of such coated drills is a factor of 4 to 6 larger than that of uncoated drills.

Progress in thin film preparation techniques has also greatly increased the possible application areas of carbides and nitrides. Important applications include erosion and corrosion resistant coatings [5, 6], but also high-temperature coatings. Since carbides and nitrides have very low temperature coefficients of the resistivity thin films of, in particular the nitrides are increasingly used as high-stability electrical resistors.
They are also used in electronic applications, e.g., as diffusion barriers in integrated circuits [8]. Since, as already mentioned, some of the nitrides have interesting superconducting properties [9] much research has been devoted to new applications of nitride coatings, e.g., Josephson junctions.

3. HOW?

Thin films of carbides and nitrides are normally prepared using either chemical vapour deposition (CVD) or physical vapour deposition (PVD) methods. In this section the two different groups of methods are discussed, the emphasis being put on the latter group.

3.1 CVD

CVD is a chemical process which takes place in the vapour phase close to or on the surface of the substrate (sample to be coated) so that the reaction product is deposited on to the substrates. Since a large number of chemical species exists in the gaseous state and many different chemical reactions are possible, depositions of many metals, semiconductors, alloys and refractory compounds can be performed by CVD. For instance, the formation of TiN can proceed according to the following reaction:

\[ 2\text{TiCl}_4 + \text{H}_2 + 4\text{H}_2 + 2\text{TiN} + 8\text{HCl} \]

This reversible reaction is endothermic, which means that in order to shift the reaction to the right energy has to be supplied. This is generally done by raising the temperature. For this particular reaction the temperature has to be raised to above 900°C, higher temperatures resulting in higher deposition rates. The deposition rate also depends of inter-diffusion of the reactants and reaction products in the gas-phase.
The high temperatures needed restrict of course the possible substrate and coating-substrate combinations. But if the substrate does not become damaged by the high temperature, an excellent adherence of the coating is usually obtained, even if problems with, e.g., brittle phases exist due to diffusion of material between the coating and the substrate.

The good "throwing power", i.e., the ability to coat irregularly shaped objects should also be mentioned as a real advantage of the process. A development of the CVD process which makes it possible to deposit at much lower temperatures is the plasma activated CVD (PACVD). In this process the molecules in the CVD gas mixture are excited by a plasma to energies above those corresponding to thermal activation. This method has been used for the deposition of both TiN and TiC films [9].

For further details of the CVD process the reader is referred to a monograph by Powell et al. [10] published in 1966 or to one of the many review articles published (see for instance Ref. [11]).

3.2 PVD

Physical vapour deposition (PVD) methods can be divided into two main groups, evaporation and sputtering. In evaporation, the coating material is transferred into the vapour phase by heating (boiling). This is normally done by heating the material with a high-energy electron beam or by resistance heating. The escaping vapour atoms will travel in straight lines until they collide with the substrate or the chamber walls, eventually condense and form a film. If a reactive gas is added during evaporation, compounds such as oxides, carbides and nitrides may be formed.

In sputtering, the coating material is transferred to the vapour phase by bombarding it with energetic inert gas ions. When these fast ions strike the surface of a material, atoms (or clusters of atoms) of the
material are ejected by a momentum-transfer process. As in evaporation, the ejected atoms can condense on the substrate and form a film. Just as in evaporation, a reactive process can be performed.

In the following, a more detailed description of the three PVD processes most commonly used for the preparation of carbide and nitride thin films will be given. For a general description of PVD processes, the reader is referred to "Handbook of Thin Film Technology" edited by L.I. Maissel and R. Glang [12], "Thin Film Phenomena" by K.L. Chopra [13] and "Thin Film Processes" edited by J.L. Vossen and W. Kern [14].

3.2.1 Activated Reactive Evaporation, ARE

ARE which was developed by Bunshah in 1971 [15] has been utilized to prepare coatings of carbides, nitrides, oxides, sulfides and related compounds. In the case of carbides and nitrides, coatings of TiC, TiN, ZrC, VC, NbC, HfC and HfN and also different mixtures of them have been produced [15-18]. The ARE process is shown schematically in Fig. 3. In this process, the metal is evaporated using an electron-beam evaporator. A reactive gas is also introduced into the chamber and a plasma initiated between a positively-biased electrode and the chamber. The metal atoms and the gas molecules in the plasma become partly ionized or excited. Thereby the probability of reaction between the gas and the metal increases (activation). The plasma is formed due to that secondary electrons created at the melt are drawn to the positively-biased electrode and "en route" cause ionization by collisions with both metal atoms and gas molecules. For deposition of nitrides, N2 is normally used but even NH3 has been tried as a reactive gas. For preparation of carbides, either CH4 or C2H2 is used. Relatively low pressures of the reactive gas can be used (<10^-3 torr). The deposition rates obtained are high (~1 μm min^-1), at least compared
Fig. 3. The activated reactive evaporation process (from R.F. Bunshah [18]).
to other methods for synthesis of carbides and nitrides. By varying the pressure of the reactive gas or the metal evaporation rate, the composition of the compound can be varied.

3.2.2 Reactive sputtering

In Fig. 4 a schematic representation of the sputtering process is shown. A high negative potential (1 to 4 kV) is applied to the target and if an inert working gas is introduced into the vacuum chamber, a glow discharge can be initiated and maintained. The ions produced in this glow discharge are accelerated towards the target and when they collide with it atoms are ejected. The gas pressures used range from a few mtorr to about 100 mtorr and the most commonly used sputtering gas is argon. The voltage applied to the target can be either d.c. or r.f. If insulating targets are used a radio frequency potential (usually at 13.56 MHz) has to be applied, a d.c offset voltage is then induced at the target surface and sputtering thus becomes possible. Due to the more efficient ionization of the working gas r.f. sputtering usually works at lower pressures. The deposition rates are generally much lower (< 1 μm min⁻¹) than in, e.g., evaporation. To enhance the degree of ionization in the plasma and the number of ions impinging at the target (and thus the deposition rate) a magnetic field can be applied parallel to the target surface. Such a magnetic field restrains both the electrons in the plasma and the primary electrons emitted from the target to the vicinity of the target and thereby increases the ionization. These cathode-target configurations are called magnetrons. Fig. 5 shows a cross-section of a planar magnetron cathode and the principles of operation.

Magnetron sputtering is of great importance in industrial applications since deposition rates up to a few μm min⁻¹ can be achieved.
Fig. 4. The basic sputtering process (from R.F. Bunshah [18]).
Fig. 5. Planar magnetron cathode.

1) Magnets, 2) cathode, 3) target, 4) magnetic field lines
6) electrons, 7) sputtered target atoms.
Uniform deposition can also be obtained over very large substrate areas (many m$^2$). As magnetron cathodes are available in various shapes, e.g., as rods (cylindrical post magnetrons) or tubes (cylindrical hollow magnetrons) sputtering on to wires, rods, tubes etc. can be performed using ideal geometries.

There has been excellent review articles published on various aspects of sputtering [19]. For different types of magnetron sputtering the reader is warmly recommended to read the articles by J.A. Thornton and A.S. Penfold, D.B. Fraiser, and R.K. Waits all three in the book "Thin Film Processes" edited by J.L. Vossen and W. Kern [14].

If a reactive gas is introduced into the chamber during the process, different compounds can be synthesized. The reactions occurring between the metal and the gas can occur on the target surface, on the substrate and in the case of high working pressures, in the gas phase. A reaction at the target surface and the formation of a compound there often result in a significant reduction in the deposition rate. Reductions by a factor of 5 to 30 are normally observed. The reactions on the targets normally start when the partial pressure of the reactive gas is as low as 1-2 percent of the total pressure used. To produce coatings of the compound partial pressures above this critical pressure have to be used. A wide variety of coatings have been sputtered and a bibliography on reactive sputtering covering work done up to 1978 is presented by J.L. Vossen and J.J. Cumo in Ref. [14].

3.2.3 Reactive Ion Plating (RIP)

Ion plating is a generic term applied to film deposition processes occurring in vacuum in which the growing film is subjected to a flux of high-energy particles. The ion plating process is shown schematically in
Fig. 6. The ion plating process (from R.F. Bunshah [18]).
Fig. 6. In the process the material is usually evaporated by an electron beam evaporator. The metal vapour passes through a gaseous glow discharge on its way to the substrate. The glow discharge is produced by putting a high negative potential (1 to 5 kV) on the substrate. The gases, usually argon and an additional reactive gas, are admitted to pressures of the order of $10^{-3}$ to $5 \times 10^{-2}$ torr. Simultaneously with the deposition, the substrate is bombarded with both argon and reactive gas ions. This bombardment causes an enhanced reaction rate and a constant cleaning of the growing film by the removal of gaseous impurities by sputtering and it is also claimed to enhance the adhesion of the coating. However, undesirable effects such as a lower deposition rate due to resputtering, large substrate heating and porous coatings may also be obtained. Porosity may be the result of working at too high pressures (see Fig. 7). To reduce the gas pressure, additional electrodes and electron-emitting filaments are used to give a sufficient degree of ionization even at lower pressures. The method is then very similar to an ARE process with biased substrates (BARE).

3.3 Structure of PVD coatings

The microstructure and morphology of thick evaporated and sputtered films have been extensively studied for a wide variety of metals, alloys and compounds. The structural model first proposed by Movchan and Demchishin [20] is shown in Fig. 7 together with a later modification by Thornton [21]. It is seen that the structure depends to a large extent on the substrate temperature, $T$, used and on the melting temperature of the material deposited $T_m$ ($T/T_m$ is called the homologous temperature). Different zones each with its own structure and physical properties, can be identified.
Fig. 7. Structural zone models for PVD coatings showing how the film structure depends on the ratio between the temperature of the substrates during deposition and the melt temperature of the material deposited. In b) the dependence on argon pressure during deposition is also shown.

a) Model proposed by Movchan and Demchishin [20].
b) Model proposed by Thornton [21].
Carbides and nitrides which are generally deposited at temperatures around and below 500°C are found to be of zone T or even zone 1 structure. The columnar structure obtained can, however, be changed with, e.g., ion bombardment during deposition. If the pressure can be kept low and a sufficiently high ion bombardment can still be maintained very dense structures are obtained. From Fig. 7, it is also seen that if too high gas pressures are used, an open type of zone 1 structure is promoted.

3.4 Adhesion of PVD coatings

Clearly a fundamental and important property of films is adhesion to the substrate. Unfortunately there is no standard recipe of making films with good adhesion. Neither is there a standard test which allows measurement and quantification of the film-substrate adhesion. However, the most commonly-used and reproducible technique is the scratch test [22]. Below, a few procedures which have been found to promote good adhesion are listed:

* Ultrasonic degreasing and cleaning of the substrate before introduction into the vacuum chamber.

* Ion bombardment of the substrate and target in the vacuum chamber before starting the deposition ("sputter cleaning").

* Degassing of substrates by using a high temperature (200-300°C)

* Deposition of thin interfacial layers of pure metals, oxides or nitrides.

Usually a combination of two or more of the procedures listed above is necessary if good adhesion is to be obtained.
REFERENCES


II EXPERIMENTAL

Since experimental details are described only briefly in each of the papers presented in this thesis, a separate chapter on this topic was felt to be needed. The chapter is divided into three parts, Apparatus (2.1), Depositions (2.2) and Analysis (2.3). The first two parts describe the apparatus and the deposition procedure used whereas the third part describes the methods for the analysis of the films. However, since some of the methods of analysis are described extensively in other chapters the emphasis in this chapter is put on the first two parts.

1 Apparatus

The apparatus which was used for depositing Ti-C, Ti-N and Ti-C-N was constructed in 1976 at the Department. The apparatus consists of a vacuum chamber, a Varian r.f.-diode sputtering unit and an evacuation pumping system. The diffusion pump is a specially-designed pump-baffle combination for sputtering applications. At the beginning of the experiments with reactive sputtering the vacuum system was complemented with a titanium sublimation pump (TSP) and facilities (IR-lamps) making it possible to bake the chamber walls. These additions were made to get a cleaner vacuum which is essential when depositing such reactive materials as titanium.

1.1 Rf-diode sputtering unit

A schematic view of the r.f.-diode sputtering system is shown in Fig. 2.1. The sputtering unit is a Varian diode sputtering unit model no. B980-2404. This unit consists of a 18" top-plate with 3 target electrodes, shutters, a substrate table and an r.f.-impedance-matching network together with an r.f. power supply model no. 980-2407. The target electrode is a
Fig. 2.1  Schematic representation of the r.f.-diode sputtering system.
flat water-cooled copper disk to which the 6" target with backing plate can be fastened by means of an integral centre screw. The electrode is flange-mounted through the top plate and surrounded by an adjustable grounded shield. The latter shield also has an adjustable skirt which helps to confine sputtering to the surface of the target. The shutter assembly consists of two independently rotating aluminium disks 15" in diameter with cut-outs. One shutter rotation knob turns the two shutter plates independently to positions located precisely beneath the targets. The use of this shutter system allows one to sputter clean first the target and then the substrates and finally to deposit. The substrate table supplied with the unit is a continuously rotatable water-cooled table. However, since substrate heating facilities were needed in this project it was replaced. A description of the substrate table actually used is given in section 2.1.2.

The r.f. power supply consists of a crystal controlled oscillator with amplifiers that applies a maximum power of 2.5 kW at 13.56 MHz to the target electrodes. To dissipate maximum power to the load, its impedance should be equal to the conjugate of the generator output impedance. Since most generators, such as the one used here, have output impedances that are purely resistive and as low as 50 ohms and r.f. discharges normally have larger and partly capacitive impedances an impedance matching network is needed. A load equal to the generator output impedance is therefore simulated by combining the discharge load with a variable matching network.

The r.f. impedance-matching network is placed directly on the top-plate. The reason for placing it as close to the discharge as possible is to avoid power losses due to the large reactive currents flowing between the network and the discharge.
The matching network is tuned for optimum use of power by measuring the input and reflected powers. Even if values as low as 2% may be obtained the reflected power typically is 5-10% of the forward power. In addition to the power applied to the plasma, the voltage on the target electrode has been measured. Both the r.f. peak to peak and the d.c. offset voltage were measured by applying a high voltage probe to the back of the target electrode and displaying the signal on an oscilloscope. Fig. 2.2 shows the behaviour of the r.f. peak to peak and the d.c. offset voltages with net power applied to the plasma.

1.2 Vacuum system

Fig 2.3 shows a schematic representation of the vacuum system. The positions of the vacuum gauges and valves are also shown. The pumping system consists of a double-stage roughing pump (Balzers DUO 120A) and an oil diffusion pump (Varian Sputt-torr 0175). The roughing pump has a pumping speed of 120 m³/h. The diffusion pump is a pump-baffle combination which has been specially designed for sputtering applications requiring inlet pressures up to 2.5x10⁻² torr. A liquid nitrogen trap is included above the diffusion pump. This both reduces the backstreaming to a minimum and greatly increases the pumping speed for water vapour. Backstreaming is also kept as low as possible by operating the diffusion pump with a polyphenyl ether oil (Convalex 10). The pumping speed of the diffusion pump is specified to be 400 l/s up to pressures as high as 10⁻² torr. However, due to the reduction in conductance by the liquid nitrogen trap and high vacuum valve the speed is reduced to 250 l/s. This pumping speed of 250 l/s was measured according to the constant pressure method [1]. In Fig. 2.4 both the specified and the measured speed are shown. It is seen from the figure that the speed does not start to fall until above 10⁻².
Fig. 2.2 Target voltage vs. net power applied. Both the r.f peak-to-peak and the dc-offset voltages are shown.
Fig. 2.3 Schematic view of the vacuum system.

1) Roughing pump, 2) Fore line trap, 3) Pirani gauges, 4) Valves
5) Diffusion pump, 6) LN$_2$ trap, 7) Dry Nitrogen for back filling
8) TSP filament, 9) IR lamps for baking, 10) Spiral for cooling water, 11) Ion gauges, 12) Mass spectrometer.
Almost all of the depositions described in this work were made at pressures below $10^{-2}$ torr where the pumping speed is constant at 250 l/s. As mentioned above a titanium sublimation pump was added to the system at the start of this work. This was done both to reduce the ultimate pressure and to obtain as "clean" a vacuum as possible. The latter effect is discussed in section 2.1.3. The ultimate pressure of this system is $5 \times 10^{-7}$ torr.

Vacuum gauges are included in the system both for safety control and for measurements of the pressure in the vacuum chamber. For the latter measurement two types of ionization gauges have been used, for pressures below $10^{-5}$ torr a gauge of the Bayard-Alpert inverted type (Balzers 1MR120) and for pressures above $10^{-5}$ torr a high-pressure ionization gauge (Balzers IMR110). Since the sensitivities of ionization gauges vary by as much as a factor of 10 for different gases [2], it should have been better to use a capacitance manometer for the higher pressures. The advantage of this type of pressure gauge is that it measures the real pressure, independent of gas type. To overcome the problem of different sensitivity factors for different gases a capacitance manometer (MKS Baratron 170) was borrowed and calibration curves for argon, methane and nitrogen recorded. Fig. 2.5 shows such calibration curve for the BA gauge. All the pressure values given in the next chapters have been corrected for sensitivities using the measured calibration curves.

The residual gases in the chamber were measured using a 180° magnetic sector mass-spectrometer (Vacuum Generators Micromass 2A). The mass-ranges in this spectrometer are 12-60 and 48-240, the lower range being that most commonly used. A detailed description of the analysis of the residual gas is given in section 2.1.3.
Pumping speed vs. pressure for the diffusion pump, both specified values without baffel and values measured in the chamber (•) being shown.

Calibration curves for the ion gauge (Bayard-Alphert) as obtained by the capacitance manometer. Results are shown for $N_2$, Ar and $CH_4$. 
In Fig. 2.6, the positions of the vacuum gauges, the mass spectrometer, the target and the gas inlets in the chamber are shown. To make as accurate pressure measurements as possible the ion gauges were placed as close to the target position as possible. In addition the gauges were oriented so as not to point directly towards the gas inlets.

1.3 Residual gases

Since impurities are known to affect the growth and the resulting properties of sputtered and evaporated films [4-6], it is essential that the residual gas composition is known. Since we have no possibility of recording mass spectra during the depositions, only mass spectra taken before and after the depositions have been studied. Examples of mass spectra are shown in Fig. 2.7. The spectra taken before starting the depositions were recorded without any reactive gas present, but with the substrates heated to a temperature of 770K. Spectra taken after the depositions were recorded about 3 minutes after stopping the flow of argon and reactive gas.

With the aid of cracking patterns for gases [3-4], the compositions of the residual gas could be evaluated. The resulting residual gas compositions are summarized in Table 2.1. Each of the values is the mean value of about 20 separate recordings. Due to the fact that the mass ranges on the mass spectrometer only extended from 12 to 60 (or 48 to 240), hydrogen and helium could not be measured. Hydrogen is probably present to a large extent.

It is seen that, with the possible exception of hydrogen, water vapour is the main constituent of the residual gas before starting deposition. Spectra taken after deposition show that the amount of water vapour present decreases during deposition. This decrease is due to gette-
Fig. 2.6 Schematic view of the positions of vacuum gauges, gas inlets and target/substrate table.
1) Target and substrate table position, 2) Ion gauges, 3) Mass spectrometer, 4) and 5) Gas inlets.
ring by titanium. This means that oxides or hydroxides could be formed in
the films. However, measurements of the residual gas composition directly
after sputter cleaning of the targets show that much of the water vapour
gettering occurs during this part of the process i.e., before the substrates are exposed to the deposition. From Table 2.1 it is also seen that
there is not only a decrease in the amount of water vapour present but
also increases in the amounts of CH₄, Ar and CO₂ (or N₂) occur during
sputtering. The increases in the amounts of Ar, CH₄ or N₂ are under-
standable since sputtering was performed in these gases. The increase in
the CO content could be explained in terms of electron and ion induced
desorption. The shutters and parts of the chamber walls are exposed to the
plasma and hence to electron and ion bombardment which can induce gas
desorption. An increase in CO content has also been observed by Andersson
[5] during sputter cleaning procedures. The effect of the titanium subli-
mation pump on some of the most common gases in the residual gas is shown
in Fig. 2.8. These measurements were all done at a partial pressure of
1x10⁻⁵ torr for the gas in question. As is seen from Fig. 2.9, other gases
constitute less than ten percent at that gas pressure. As the TSP was
operated at a constant power of 500W (50A, 10V) the curves in Fig. 2.8
give a comparison of the gettering effect of different gases. As can be
seen the gettering effect varies for the different gases with oxygen being
gettered by the titanium most readily and argon not gettered at all. The
results are summarized in Table 2.2 where the times taken to fall from
initial value to the new steady state value are given together with the
steady state values as a percent of the initial ones. The most noticeable
effect is the low gettering of methane. In fact an increase in the methane
content is observed during the first minutes of operation implying that
the pump should be operated for at least 4 minutes in order to obtain
2.7 Mass-spectra recorded at a pressure of $2 \times 10^{-6}$ torr
a) Recorded before deposition
b) Recorded 3 min after deposition with $P_{CH_4} = 2 \times 10^{-4}$ and, $P_{tot} = 5 \times 10^{-3}$ torr.

2.8 Change in reactive gas content when operating a titanium sublimation pump. The pressures were in all cases $1 \times 10^{-5}$ torr. The arrows denote the time when the TSP was started.
Table 2.1 Composition of the residual gas before and after deposition.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Dominant mass peak</th>
<th>Composition of the residual gas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before the deposition started</td>
<td>After deposition in Ar and CH$<em>4$ $P</em>{CH_4} = 1 \times 10^{-5}$ torr</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2</td>
<td>not measured</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>18</td>
<td>70</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>11</td>
</tr>
<tr>
<td>N$_2$</td>
<td>28</td>
<td>10</td>
</tr>
<tr>
<td>O$_2$</td>
<td>32</td>
<td>2</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>44</td>
<td>8</td>
</tr>
<tr>
<td>various hydrocarbons</td>
<td>26, 27, 29, 43, 57</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 2.2  Effect of the TSP on the partial pressures of various gases. All measurements have been performed with the partial pressure of the reactive gases equal to $1 \times 10^{-5}$ torr when starting the TSP.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Time required to fall to steady state (min)</th>
<th>Steady state value in % of initial value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.1</td>
<td>45</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.7</td>
<td>39</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.9</td>
<td>63</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.2</td>
<td>20</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2.7</td>
<td>93</td>
</tr>
</tbody>
</table>
2.9 Mass-spectra recorded with a reactive gas of pressure $1 \times 10^{-5}$ torr present in the chamber

a) CH$_4$ and b) N$_2$. 

$P_{CH_4} = 1 \times 10^{-5}$ torr

$P_{N_2} = 1 \times 10^{-5}$ torr
the optimum results. During the experiments, the pump was operated for 5 minute periods. Fig. 2.9 shows that the reactive gases constitute about 90% of the gas composition at a pressure of $10^{-5}$ torr. The majority of the experiments reported has been carried out with higher partial pressures of the reactive gases than $1 \times 10^{-5}$ torr.

1.4 Substrate holder

A simple substrate holder capable of maintaining a constant substrate temperature of between 670 and 970K during the depositions was built for this project. The substrate surface was located 4 cm below the target surface. A schematic drawing of the holder is shown in Fig. 2.10. It consists of a resistive tungsten heater. The temperature was measured using a chromel-alumel thermocouple point-welded to the surface of a dummy substrate placed on the substrate holder. The temperature is regulated by manually varying the power applied to the heater. Powers up to 1.3 kW can be used. Due to effects of plasma heating it has only been possible to obtain stable temperatures (±5%) above 670K. The main part of the depositions were carried out with the substrates kept at 770 K. The choice of this temperature was governed by the fact that grain growth and hence loss of hardness occurs in substrates of high speed steels if the deposition temperature exceeds the annealing temperature, which is normally about 830 K. Since coatings of TiN and TiC on high speed steels are of great technical importance, the deposition temperature was chosen so that the results should be applicable in such cases.
2.1 Target

The target consists of a 2 mm thick titanium sheet bonded to a copper backing plate. The titanium sheet used has a purity of 99.95% and the main impurities are oxygen and iron. As mentioned earlier the diameter of the target is 15 cm (6"). The grounded shield, the purpose of which is to restrict ion bombardment and sputtering to the target only, decreases the area from which material is sputtered at a uniform rate. In Fig. 2.11 the thickness uniformity as a function of position is shown. The values are obtained for sputtering of titanium in argon at a pressure of $5 \times 10^{-3}$ torr. The substrates were located 4 cm below the target. During reactive sputtering processes, reactions occurring on the target surface are of great importance. To be able to study these reactions in more detail the centre part of the target has been made in the form of a small plate of titanium which could be screwed into the target. This plate could be removed and replaced after each deposition. Thereby it was possible to study the composition and chemical state of the surface layers formed on the targets.

2.2 Substrates

Four different types of substrates were used, steel, copper foils, alumina and quartz. The reason for using four different types of substrates was to make the analysis of the films easier. Thus, for example, electrical measurements were made on films deposited on the insulating substrates alumina and quartz. Optical measurements were performed on films deposited on quartz which is optically a well-characterized substrate. Copper foils made the x-ray diffraction analysis easier, since x-rays are transmitted.
Ceramic insulators

Resistive tungsten heater

Water cooled copper heat reflector

Table with adjustable height

Fig. 2.10 Substrate holder

Fig. 2.11 Film thickness as a function of position on the substrate holder.
through both the substrate and the film. Using different types of substrates it is also possible to study the effect of the substrate material on the film properties by measuring the same properties on films deposited under identical conditions but on different substrates.

The steel substrates, SIS 1311 (Fe-0.12C-0.05Si-0.7Mn-0.08P-0.06S) were in the form of disks with diameters of either 19 mm or 25 mm and a thickness of 4 mm. These substrates were ground and polished with 1 μm diamond paste in the final stage. The alumina substrates (25 x 25 mm) and the quartz disks with diameter 25 mm were both 1 mm thick. The copper foils were 7 μm thick. To avoid diffusion of copper into the films the copper foils had to be coated with nickel to a thickness of one to three micrometers. The steel, alumina and quartz substrates were cleaned ultrasonically for 10 minutes in each of trichlorethylene, acetone and ethanol. The alumina and quartz substrates were prior to cleaning scrubbed with tissue paper in soap and water. Since the copper foils could not be cleaned ultrasonically without wrinkling they were simply dipped in ethanol for 5 - 10 minutes.

After cleaning the substrates were weighed to an accuracy of ± 0.05 mg so that the gain in weight and hence the density of the films deposited could be derived.

2.3 Deposition procedure

After the substrates had been cleaned and weighed they were put on to the substrate table. Copper foils were clamped to the substrate table using stainless steel clamps. To ensure that they were at the same distance from the target and had the same substrate temperature as the other types of substrates they were placed on a piece of alumina. Electrical contact to the substrate table was provided by the stainless steel clamp.
When the chamber was exposed to air its walls were heated by the IR lamps positioned in its bottom. This was done in order to decrease the sorption rate and to increase the desorption rate. This baking of the chamber walls was also continued for the first hours of the evacuation period. The evacuation was in all cases made over night and was continued until the pressure was below $2 \times 10^{-6}$ torr. Towards the end of this period the TSP was operated for a couple of 5 minute periods. When the substrate was heated the pressure started to rise. However, within one to two hours when the substrate temperature was 770 K the pressure was in most cases below $2 \times 10^{-6}$ torr. Depositions were not carried out unless the pressure was below $3 \times 10^{-6}$ torr.

Argon was then bled into the chamber to a pressure of $1 \times 10^{-2}$ torr. With the shutters in the presputtering position the target was presputtered for 15 minutes at a net power of 500-700 watts. The chamber was then evacuated and the partial pressure of the reactive gas set to the desired value. Since we had no means of controlling the partial pressure during the sputtering sequence a deposition was accepted only if the partial pressure had not changed after deposition was completed. Since high-precision needle-valves was used and the pressure in the gas inlet system was kept constant only minor fluctuations in the pressure were observed. After the partial pressure had been set to the desired value, argon was let in until the total pressure chosen was reached. A plasma was then initiated and the net power set to the desired value which in most depositions was 1kW. The shutters were then put in the position for deposition and the power adjusted so as to obtain the right power-level with the reflected power minimized. Depositions were continued for one to three hours giving film thickness ranging from 2 to 7 μm. Some depositions made for optical measurements were only deposited to thicknesses between
400Å and 3000Å. To keep the reproducibility as high as possible, the same procedure was followed in each deposition.

3 Analysis

This section describes the methods and procedures used for the different types of analysis performed on the films. In most cases, only short summaries are given since detailed descriptions are included in later chapters and in references.

3.1 Thickness and density measurements

To be able to determine deposition rate, density and electrical resistivity it is essential that the film thicknesses are determined as accurately as possible. For films with thicknesses larger than 1 μm, two independent methods have been used, measurements of cross sections of the films in a scanning electron microscope and determinations of the height of a step using a Talysurf 4. A description of how the cross-sections were prepared is given in section 2.3.2. When a step height is measured using a talysurf, the surface roughness of the substrate and the deposited film should be as small as possible so as to obtain maximum accuracy. Because of this, the step was produced on substrates of quartz. A typical step profile is shown in Fig. 2.12. Using these two methods, the accuracy of measurement in the range of thickness 1-7 μm is estimated to be 5%. For films deposited to thicknesses less than 1 μm, a multiple interference microscope (CEJ Multim 3000D) with monochromatic mercury light (λ = 5460Å) has been used for the thickness determinations.

By combining the results of thickness measurements and weight gain measurements, the densities of the films were obtained. The weight-gain
measurements were performed on a high precision microbalance with a specified accuracy of 0.01 mg. However, since the balance is not located in a temperature- and humidity-controlled room, the actual accuracy is only about 0.05 mg.

The accuracy of the density measurement are estimated to be of the order of 10%.

3.2 Morphology

The morphologies of the deposited films were studied using a scanning electron microscope (Cambridge Stereo Scan 180). During the main part of the experiments the microscope was operated with an accelerating voltage of 20kV. Both the surface and the cross sections of the films were studied. Surfaces were studied on films deposited onto polished steel substrates. Cross-sections were studied both on substrates of steel and alumina. The cross-sections of films deposited on steel substrates were prepared by sawing from the rear side, almost down to the film and then fracturing the substrate and the film. To be able to obtain a brittle fracture in the steel the samples were cooled to liquid nitrogen temperature before being broken. Alumina substrates were broken by first making a scratch on the rear side with the aid of a glass cutter and then fracturing.

3.3 Composition

When studying thin films of alloys or different compounds such as carbides and nitrides it is essential that purity, chemical state and composition are determined. In the particular case of carbides and nitrides the task of composition determination is a difficult one especially for thin film samples, since small masses make the use of conventional methods of chemical analysis almost impossible. In this work, analysis was made
using Auger electron spectroscopy and energy-dispersive electron-microprobe investigations. A detailed description of the quantification of these measurements and of the experimental equipment used is given in chapters 3 and 5.

3.4 Crystallographic structure

Crystallographic structures and interplanar distances were studied using x-ray diffraction.

The x-ray diffraction experiments were performed using a Guinier camera and CuKα1 radiation. The Guinier camera used is described in more detail by Hentzell [6]. Films were analysed as deposited on 7 µm thick copper foils. In some cases where the diffraction lines from the film and the copper substrate interfered, the copper was dissolved in nitric acid and the free standing film was analysed. No effect of the nitric acid on the films was noticed. KCl powder was also analysed together with the coating to obtain an internal calibration.

The complete x-ray diffraction spectrum from a δ-TiN phase film is shown in Fig. 2.13 and an enlargement showing the TiN (111) and KCl (220) peaks is given in Fig. 2.14. In some cases the peaks have been smaller and less well-defined. This has especially been the case for TiC films and films deposited to small thicknesses. An example of broad, poorly-defined peaks is shown in Fig. 2.15. The interplanar spacings were determined using the method described by Hentzell [6]. This method gives values of interplanar spacings with an accuracy of better than ± 0.001Å. From the obtained interplanar spacing \( d_{hkl} \), the lattice parameter was calculated by multiplying each \( d_{hkl} \) by \((h^2 + k^2 + l^2)^{\frac{1}{2}} \) and taking the mean value.

Line broadening of diffraction peaks is caused by instrumental setup, size of the crystallites and lattice imperfections present in the material.
Fig. 2.12 A surface profile as recorded by a Talysurf showing a step produced during the deposition of TiN on a quartz substrate.

Fig. 2.13 X-ray diffraction spectrum of a TiN film. Peaks from the copper substrate and the KCl are also seen.
Fig. 2.14 Enlargement of a part of Fig 2.13 showing the TiN(111) peak at the Bragg angle $\theta$ and the KCl (220) peak.

Fig. 2.15 Two poorly-defined peaks from TiC(200) and TiC(111).
being analysed. The instrumental broadening was measured on well-defined KCl peaks, and subtracted quadratically from the observed line breadth following the procedure described by Klug and Alexander [7]. If at least two reflections are present, both the crystallite size and the lattice strain caused by imperfections can be calculated using the Fourier method of Warren and Averbach [8]. If no or only small amounts of imperfections in the grains are present the grain size D can be calculated using the Scherrer equation [9]

\[ D = \frac{K \lambda}{\beta_{hk1} \cos \theta} \]

where K is the Scherrer constant, \( \lambda \) the x-ray wavelength, \( \theta \) the Bragg angle and \( \beta_{hk1} \) the full line width at half maximum after correction for instrumental broadening.

The intensities of the diffraction lines were measured as relative intensities (peak heights) by setting the most intense reflection to 100.

3.5 Hardness

Since because of their high hardnesses carbides and nitrides are used extensively in commercial applications we have measured the Vickers hardness values of the films produced. Furthermore hardness is a fairly easily measurable and reproducible quantity, which also can give information about other mechanical properties of the film. It has for example been shown [10,11] that hardness values can be related to the yield strength (\( \sigma_y \)) by a simple relation of the form \( H = A \sigma_y \) where A is an empirical constant.
In this work we have measured the Vickers hardness values using an optical microscope (Carl Zeiss Jena Neophot 2) equipped with a Vickers indentor. The reliability of the measurements was established by making measurements at different loads and making a large number of indentations. At least 10 indentations at each load and at a loading time of 10-20 s were used. Hentzell [6] has shown that if the ratio between film thickness and depth of indentation exceeds four the hardness value is unaffected by the substrate hardness. These measurements were made on nickel-aluminum films with hardmesses ranging from 30 to 800 Vickers. In Fig. 2.16 results are shown for different Ti-N films with hardness ranging from 300 to 2000 Vickers. From the figure it is obvious that the measured film hardmesses are unaffected by the substrates if the ratio between the film thickness and the indentation depth exceeds five. This result is in good agreement with the results for Ni-Al films obtained by Hentzell [6]. The hardness values presented later in this thesis are all obtained with the ratio between the film thickness and the indentation depth exceeding 5. All the values presented in the text or figures were obtained at a load of 10p.

3.6 Electrical resistivity and optical properties

The electric resistivity and its variation with temperature can yield information not only about the electric properties of the material but also about its impurity content, stoichiometry and porosity [12]. It is thus important that these quantities are measured in order to be able to characterize the material in detail. In this work we have measured the resistivity using a standard four point probe. The temperature coefficient of resistivity was measured by recording the change in resistivity while cooling the sample to liquid nitrogen temperature.
Measured values of the Vickers hardness for different films of Ti-N as a function of the ratio between film thickness and depth of the indentation. The hardness of the substrate is shown by the dashed line.
The optical properties of the films have been studied by recording reflectance spectra. Both specular- and diffuse-reflectance have been studied. These measurements have been performed in collaboration with Uppsala University. The results is not presented in this thesis, but the results could be found in Refs. [14, 15].
REFERENCES


In order to understand the growth and the resulting properties of thin films of carbides and nitrides, it is essential that their composition is known. This paper describes quantitative Auger analysis of the Ti-C, Ti-N and Ti-C-N systems, based on relative sensitivity factors, determined using both peak height plots and standard samples. The relative sensitivity factors were found to be independent of composition and agreement between the values obtained with the two methods being very good. Matrix effects on escape depth, backscattering, atomic density, peak shape and preferential sputtering are discussed. The effect of preferential sputtering in the Ti-C and Ti-N system was determined. The results show that no preferential sputtering occurs in the Ti-C system whereas a small effect was observed in the Ti-N system. At N/Ti ratios below 0.8, Ti is preferentially sputtered and for higher ratios, N is sputtered preferentially.
INTRODUCTION

Thin films of carbides and nitrides have become a rapidly expanding field of interest during the last few years [1, 2, 3]. To understand the growth and resulting properties of these types of film it is essential that, e.g. their crystal structure, chemical composition and defect structure are known. This paper reports studies of the chemical composition of reactively sputtered titanium-carbide, -nitride and -carbonitride films using Auger analysis.

Characterization of chemical composition of carbides and nitrides, including nonmetal-to-metal ratio and impurity content is a difficult problem. Chemical methods used for this task include for instance combustion techniques, coulometric techniques and different kinds of spectroscopic analysis [4, 5]. Common to all these techniques is the fact that the amount of material needed is rather large, which restricts their use to bulk samples. Chemical methods of determining the composition of thin film samples have, however, also been tried [6, 7]. Chevallier et al. [6] used a microchemical determination of the composition of TiN films. At least 50 mg of the sample was needed but the accuracy of the method was still estimated to be worse than 20%.

A number of problems are also associated with the use of energy-dispersive electron-microprobe analysis for determining the composition of carbides and nitrides. Due to the fact that carbon and nitrogen both have low X-ray yields [8] and that detector efficiency for C and N X-rays is almost zero [9], it is difficult to analyse these elements using this technique. For samples that are free from impurities and only contain carbon or nitrogen besides the metal it
is possible to calculate the concentrations of the non metallic elements by a difference method. Since the probe depth is about 3-4 μm when accelerating voltages of 10-30 kV are used restrictions are also put on the thicknesses of the films being analysed. The need for films thicker than the probe depth is accentuated when the substrates consist of heavier atoms than those present in the films. This is due to the fact that the X-rays excited from the substrates produce fluorescence radiation in the films resulting in errors in the determined values of composition.

Chemical analysis of surfaces and surface regions by electron spectroscopic methods such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS or ESCA) are today almost routine operations. However, the use of these methods for quantitative analysis is difficult, especially when the sample contains many elements with large differences in atomic mass or electronic structure. The use of these techniques as quantitative tools can proceed mainly in two directions, either by making use of reference data bases with known relative sensitivity factors or by direct measurements on a set of reference samples with known compositions. The latter method is generally more accurate, since an error of less than 5% can often be achieved [10, 11]. The preparation of standards with surface topography similar to that of the unknown sample is often tedious and difficult and in many cases simply impossible. For these reasons, the use of tabulated sensitivity factors is often preferable. However, the use of tabulated sensitivity factors, e.g. those given by Davis et al. [12], gives accuracies in the range 30-50% which is in many cases insufficient. The reason for the low accuracy found using these sensitivity factors is that the influence of the matrix on escape depth, electron backscattering, atomic density,
sputtering induced effects and peak shape are ignored. Since escape depth, backscattering factors and atomic densities can be calculated, matrix correction factors for these parameters can be derived. Hall and Morabito [13] have in this way calculated matrix correction factors for different combinations of 55 elements. Mathieu and Landoldt [14] have also studied matrix correction factors by comparing calculated values with experimental results for several binary alloys.

The aim of this paper is to develop relative sensitivity factors which could be used for quantification of AES data obtained from Ti-N, Ti-C or Ti-C-N samples. The effects of matrix corrections in these systems are also discussed.

2 EXPERIMENTAL DETAILS

2.1 Sample preparation

The samples were prepared using reactive sputtering. Titanium (99.99%) was r.f.-sputtered in mixed Ar-CH₄, Ar-N₂ and Ar-CH₄-N₂ discharges. To obtain samples with as wide a composition range as possible, the amounts of the reactive gases were varied between 0 and 100%. The depositions were carried out in a vacuum system equipped with a special diffusion pump-baffle combination (Varian Sputtorr 175) capable of maintaining a constant pumping speed of 250 l/s up to pressures as high as 1.5·10⁻² torr. A titanium sublimation pump was also used in order to get as clean a vacuum as possible. The pressure obtained before gases were admitted was about 5·10⁻⁷ torr. The depositions were carried out at a total pressure of 5·10⁻³ torr. The r.f. net power density was kept constant at 5.7 W/cm² which is equivalent to a current density of 1.5mA cm⁻². Substrates of polished steel and quartz
were maintained at a temperature of 775 K during deposition and films were deposited to thicknesses in the range 0.2-7 μm.

2.2 Analysis

The AES experiments were performed in a commercial instrument (Varian CMA/LEED Console Fast Cycle System, 981-2001) with a base pressure of $10^{-9}$ torr without baking, this pressure being reduced to $1\cdot10^{-10}$ torr after a bake-out at 200°C. All the experiments were carried out with an electron beam having a kinetic energy of 3 keV and a current of 2.5 μA. The resolution of the single pass CMA used is 0.25%. A modulation voltage of $2V_{p-p}$ was applied to the analyser and the spectra were recorded with a 5 eV s$^{-1}$ scan speed. In order to remove the outermost surface layer of contaminants, ion etching was used. It was performed using argon gas (99.9995%) at a pressure of $5\cdot10^{-5}$ torr. To ensure uniform etching the beam was slightly rastered. The energy of the ions was kept at 3 keV and the ion current density at 0.1 mA cm$^{-2}$. The incidence angle of the beam was 70°.

The crystallographic structure of the different samples was determined by the use of X-ray diffraction analysis. The diffraction patterns were recorded with a Guinier camera using filtered CuK$_{α1α2}$ radiation.

3 RESULTS AND DISCUSSION

3.1 AES spectra

Figs 1-3 show the changes observed in differentiated AES spectra of Ti when carbon and nitrogen are added. As can be seen from Fig 1 the strong Ti lines at 418 and 387 eV (arising from L$_{3}M_{2,3}$ and
shake-up \( L_{3}M_{2,3}M_{4,5} \) transitions respectively [15]) decreases with increasing carbon content. In pure Ti samples, a relatively strong peak at 383 eV with only a small positive excursion \( (L_{3}M_{2,3}M_{2,3}) \) is observed. When the carbon content increases it is seen that the form of this peak changes, the positive excursion becoming larger. For the Ti peak at 418 eV no such large change in peak shape is observed and in particular there is no change in line width, as measured as the separation between the positive and negative excursions of the peak. Neither is a change in linewidth observed for the C KLL peak at 270 eV. In view of this the Ti 418 eV peak and the C 270 eV peak can be used for quantitative analysis without any corrections for peak shape changes with concentration.

In the case of the Ti-N system, quantification of the results is complicated by the fact that the main Auger electron emission from nitrogen \( (KL_{2,3}L_{2,3}) \) occurs at an energy of 381 eV overlapping with the \( L_{3}M_{2,3}M_{2,3} \) transition from Ti. From Fig 2 it can also be seen that a peak gradually develops at 413 eV as the nitrogen content increases. This peak can be attributed to a cross transition of the type \( (TiL_{3})(TiM_{2,3})(NL_{2,3}) \). The energy difference between this peak and the \( TiL_{3}M_{2,3}M_{4,5} \) peak is calculated to be 5 eV by using binding energies from Coughlan and Clausing [16]. The energy difference observed is in excellent agreement with the calculation. Similar behaviour is observed for the \( TiL_{3}M_{4,5}M_{4,5} \) peak at 450 eV, a peak arising from \( (TiL_{3})(TiM_{4,5})(NL_{2,3}) \) appearing at 445 eV as the amount of nitrogen increases. These cross transition peaks appear initially as shoulders on the Ti peaks and do not develop fully until the film consists of the \( \delta \)-TiN phase. The facts that the main nitrogen peak overlaps with peaks from titanium and that cross transitions occur, one of which
Fig 1 Typical differentiated Auger electron energy spectra of Ti-C samples. Spectra are shown for four different values of the C/Ti ratio.
Fig 2 Typical differentiated Auger electron energy spectra of Ti-N samples. Spectra are shown for four different values of the N/Ti ratio.
appears at the same position as the positive excursion of the 418 eV
titanium peak, make quantification difficult. As is seen from Fig 2
the TiL\textsubscript{2,3}N\textsubscript{2,3} peak at 383 eV has a small positive excursion located
at 379 eV which also interferes with the nitrogen peak. However, the
amount of nitrogen can be represented by the positive excursion (at
377 eV) from the NKL\textsubscript{2,3}L\textsubscript{2,3} transition with the part originating from Ti
subtracted. This subtraction is especially important when samples
with small amounts of nitrogen are analysed. The amount of titanium in
the samples can be represented by the negative excursion of the Ti
peak at 418 eV.

For the ternary system Ti-C-N, (see Fig 3), the analysis is even
more complicated since apart from the nitrogen titanium peak overlap
at 377 eV, the carbon induces a growth of the positive excursion of
the Ti peak at 383 eV as discussed earlier. This positive part is
located at 378 eV and hence interferes with the positive excursion of
the nitrogen peak. The significance of this in quantitative analysis
is discussed later.

3.2 Sensitivity factors

The peak to peak height in a derivative spectrum due to an Auger
transition (wxy) associated with element i can be written as [10, 17]

\[ H_{\text{wxy}} = C_i N (1+r_x)^{\lambda_x} \sigma_{x}^{\gamma_{x}} f_{x}^{k} \] (1)

where \( C_i \) is the atomic fraction of element i in the sample which
has to be uniform over the volume being analysed, N the total number
of atoms per unit volume, \( 1+r_x \) the backscattering correction factor,
\( \lambda_x \) the effective escape depth of the electrons, \( \sigma_{x} \) the ionization
cross-section of level w, \( \gamma_{x} \) the wxy Auger transition probability, \( f_{x} \)
Fig 3  Typical differentiated Auger electron energy spectra of Ti-C-N samples. Spectra are shown for four different compositions.
the "peak shape" factor and \( k \) the spectrometer factor. The spectrometer factor includes the effects due to instrument transmission and the primary current and energy. To convert measured peak heights to concentrations either tabulated elemental sensitivity factors with respect to silver [12] or relative sensitivity factors as defined by Hall and Morabito [18] can be used. In the latter case, the relative sensitivity factor for a binary alloy AB is defined as \( (H_A/C_A)/(H_B/C_B) \) where \( H_A \) is the peak height for a transition associated with element A and \( C_A \) the atomic concentration of element A. Since peak heights are normally measured after sputtering (denoted by an "s" superscript in the following) a sputter correction factor has also to be included in the analysis. This correction factor can be defined as

\[
R_{A,AB} = C_A^s/C_A
\]  

Using equation (1) and the fact that \( C_A + C_B = 1 \) the peak height for a transition in element B after sputtering can be written as

\[
H_B^s = N (1 + r_{B,AB}) \gamma_B \gamma_B^B k_B R_{B,AB} - \frac{(1 + r_{B,AB}) \gamma_B \gamma_B^B k_B R_{B,AB}}{(1 + r_{A,AB}) \gamma_A \gamma_A^A T_{A,AB} R_{A,AB}} \cdot H_A^s
\]  

From the definition of the relative sensitivity factor it is seen that equation (3) can be written as

\[
H_B^s = N (1 + r_{B,AB}) \gamma_B \gamma_B^B k_B R_{B,AB} - \rho_{rel} \cdot H_A^s
\]  

with

\[
\rho_{rel} = \frac{(1 + r_{B,AB}) \gamma_B \gamma_B^B k_B R_{B,AB}}{(1 + r_{A,AB}) \gamma_A \gamma_A^A T_{A,AB} R_{A,AB}}
\]
If then $H_B$ is now plotted vs. $H_A$ an indication of the variations in $p_{rel}^S$ with composition can be obtained. A linearity of such a plot does not deny matrix effects since a change in one matrix variable could be compensated for by an opposite change in another variable. If a straight line is obtained the relative sensitivity factor can be calculated from the slope. Figs 4 and 5 show such plots for the Ti-C and Ti-N systems respectively. Due to the fact that only the negative part of the Ti 418 eV peak has been used in the Ti-N system the peak heights for pure Ti in the two cases are not comparable. From the figures it is seen that good linearities are obtained. However, in the Ti-C system, films consisting of pure carbon or carbon with small amounts of titanium do not fall on the straight line. This is understandable since the form of the carbon peak in these cases is quite different from that when the carbon is in the carbide phase. A typical graphite appearance of the carbon peak is found in the carbon-rich region of the system. In the case of the Ti-N system it is impossible to make films with a higher nitrogen content than approximately 55 at. % [4]. The sensitivity factors (as measured from the slope) are $p_{rel}^S(C,Ti) = 0.95$ and $p_{rel}^S(N,Ti) = 1.19$. These values can be compared with the results of direct measurements of the sensitivity factors performed on bulk standard TiC$_{0.98}$ and TiN$_{0.83}$ samples. These measurements gave values of the relative sensitivity factors of $p_{rel}^S(C,Ti, C/Ti = 0.98) = 1.00$ and $p_{rel}^S(N,Ti, N/Ti = 0.83) = 1.23$. Very good agreement is thus obtained between the sensitivity factors obtained with the two methods. Hall and Morabito [18] have also calculated the relative sensitivity factor for the N-Ti system and found a value of 1.20, but they do not state how the measurements of the peak heights were performed.
Fig 4 Carbon peak height vs. titanium peak height for different Ti-C samples.
Fig 5 Nitrogen peak height (positive excursion at 377 eV) vs. titanium peak height (negative excursion at 418 eV) for different Ti-N samples.
In the case of a ternary system, the same procedure as that described above can be applied using $C_A + C_B + C_C = 1$. However, at least two sensitivity factors are needed, in the Ti-C-N system for instance $P_{rel}^S(C,Ti)$ and $P_{rel}^S(N,Ti)$. Since it is not possible to use the whole Ti 418 eV peak for the quantification, due to cross-transition interference as discussed earlier, $P_{rel}^S(C,Ti) = 0.95$ as already calculated can not be used. A plot of the carbon peak height versus the height of the negative excursion of the Ti 418 eV peak yields a value of 1.62 for $P_{rel}^S(C,Ti)$. Using this value and 1.19 for $P_{rel}^S(N,Ti)$ the composition can be calculated. However, if the peak heights are plotted against each other, (see Figs 6 and 7), a slight deviation from linearity is observed in the plot of carbon versus nitrogen. From Fig 6, it is also seen that the titanium peak height is almost independent of the other peak heights in the samples analysed. The deviation from linearity in the carbon/nitrogen plot can be explained by changes in the peak shape factor with composition. As already mentioned the positive excursion at 378 eV in the Ti-C system increases when the carbon content increases. A plot of this increase relative to the carbon peak for different values of carbon to titanium peak-height ratios is given in Fig 8. Using this the nitrogen peak in the Ti-C-N samples can be corrected for the carbon induced increase of the peak. Nitrogen peak heights corrected in this way are plotted versus carbon peak heights in Fig 9. It is seen that the linearity is better and that $P_{rel}^S(C,N) = 1.40$.

By definition

$$P_{rel}^S(C,N) = P_{rel}^S(C,Ti) \cdot P_{rel}^S(Ti,N)$$

and
Fig 6 Carbon peak height (•) and nitrogen peak height (○) vs titanium peak height for different Ti-C-N samples.
Fig 7 Carbon peak height vs. nitrogen peak height for different
Ti-C-N samples.
Fig 8 Carbon induced growth of the positive excursion (located at 377 eV) of the titanium 383 eV peak. The ratio of the positive 377 eV peak and the carbon peak is plotted vs. the ratio between the carbon and titanium peak heights (negative excursion of the Ti 418 eV peak). $H_{377+}^S$ is given with the part originating from pure Ti subtracted.
$P_{rel}^{S}(C,N) = 1.40$

Fig 9  Carbon peak height vs. nitrogen peak height for some Ti-C-N samples after correction for carbon induced growth of the positive 377 eV peak.
This gives \( p_{\text{rel}}^S(C,N) = \frac{1.62}{1.19} = 1.35 \) which agrees quite well with the value 1.40 obtained above.

### 3.3 Matrix effects

As mentioned above the linearity of the peak height plots does not deny matrix effects. However, if any of the variables changes with composition, there must be a compensating change in another variable so as to maintain linearity. Changes in different variables that may occur will be discussed in the following. To a first approximation the escape depth of electrons from one component in a binary alloy can be expressed in terms of the escape depth in the pure components [19]

\[
\lambda_{A,AB} = \lambda_{A,B}^C (\lambda_{A,A} - \lambda_{A,B})
\]

The escape depth in the pure components can be derived according e.g. to Penn [20] or Seah and Dench [4]. In this work, we have used the method proposed by Seah and Dench since the RMS scatter factor obtained using their method is lower than that for Penn [20]. It is still as large as 1.36, which means that the values of \( \lambda \) obtained are rather uncertain but since ratios are used systematic errors are reduced. In order to perform the calculations atomic densities have to be known. Since the interest is concentrated on samples from the pure metal up to stoichiometric carbides or nitrides, the atomic densities of carbon and nitrogen have been calculated as the densities of these elements in stoichiometric titanium carbide and nitride respectively. The atomic densities and the calculated escape depths are given in
Table 1. Using these values, the ratios $\lambda_{N,TiN}/\lambda_{Ti,TiN}$ and $\lambda_{C,TiC}/\lambda_{Ti,TiC}$ were calculated as functions of composition. The results are shown in Fig 10 where it is seen that while the ratio between the escape depths is constant for the Ti-C system it increases slightly in the Ti-N system when the N/Ti ratio increases.

A linear approximation for the variations in the backscattering factors can also be applied

$$r_{A,AB} = r_{A,B} + C_A (r_{A,A} - r_{A,B})$$

(7)

Numerical values of the different backscattering factors can be calculated according to the procedure given by Reuter [22]. The values obtained are also given in Table 1 and the relevant ratios are shown in Fig 10. There it is seen that for both the Ti-C and Ti-N systems the ratio is fairly constant over the entire composition range.

A third matrix factor that may change with composition is the peak shape factor $f_x$. We have, however, as already been shown, taken the existing variations within the composition range examined into account. The last factor that must be considered is the sputter correction factor. When bombarding with ions preferential sputtering can occur in a sample containing elements with different sputtering yields. The material with the highest sputtering yield is preferentially sputtered, resulting in a deficiency of that element at the surface. The deficiency increases until steady state is reached. Shimizu et al. [23] and Werner and Warmholtz [24] have calculated the fractional surface coverages assuming steady state conditions. According to the model used in Ref. [24], the fractional surface coverage for the component A at time t is given by

$$\theta_A(t) = (\theta_A(0) - \theta_A(\infty)) e^{-t/\tau} + \theta_A(\infty)$$

(9)
Table 1  Atomic densities, escape depths and backscattering factors for the Ti-C and Ti-N systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Element</th>
<th>Atomic density (nm(^{-3}))</th>
<th>Escape depth (nm)</th>
<th>Backscattering factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Atomic density (nm(^{-3}))</td>
<td>Escape depth (nm)</td>
<td>Backscattering factor</td>
</tr>
<tr>
<td>TiC</td>
<td>Ti</td>
<td>56.6</td>
<td>1.17</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>122.9</td>
<td>0.62</td>
<td>1.16</td>
</tr>
<tr>
<td>Ti-N</td>
<td>Ti</td>
<td>56.6</td>
<td>1.17</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>111.8</td>
<td>0.78</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Fig 10  Escape depths and backscattering ratios as functions of composition for Ti-C and Ti-N systems.
where $\theta_A(0)$ and $\theta_A(\infty)$ are the fractional coverages at $t = 0$ and $t = \infty$ respectively and $\tau$ is a time constant. The ratio between the coverages at steady state for component A and B in a binary compound is given by

$$\frac{\theta_A(\infty)}{\theta_B(\infty)} = \frac{S_B C_A}{S_A C_B}$$

(10)

where $S_A$ and $S_B$ are the sputtering yields and $C_A$ and $C_B$ the bulk concentrations of components A and B respectively. Since the sputtering yield for a component in a compound is not expected to be the same as for the pure element [25, 26] and since furthermore, the yield may vary over the composition range the use of equation (10) with pure elemental sputtering yields is doubtful.

In this work we have studied the effect of preferential sputtering in the Ti-C and Ti-N systems by determining the changes in the C/Ti and N/Ti peak height ratios during sputtering. Since the surfaces of the samples were contaminated with oxygen and carbon and in some cases sulphur and chlorine the results obtained during the first half minute of sputtering are excluded. Also, only samples which were free from impurities (< 2 at.% after this period are used in the analysis. Fig 11 shows the change in N/Ti and C/Ti peak height ratio with sputtering time. As can be seen from the figure preferential sputtering seems to occur in the Ti-N system but not in the Ti-C system. From the data obtained and by the use of equation (9) the peak height ratios at the surface before sputtering were calculated. These values were also compared with direct measurements of these ratios before sputtering. Good agreement was found for samples with N/Ti ratios of 1.17 and 1.10 and for C/Ti ratios of 0.76 and 1.02. These samples have a single phase $\delta$-TiN or TiC structure (as determined by X-ray diffraction)
Fig 11 Change in carbon to titanium (a) and nitrogen to titanium (b) peak height ratios with sputtering time for different compositions.
and the ratios seem to be insensitive to contaminants. However, as soon as free titanium is present in the samples no correlation between the calculated and the observed ratios is found. In those samples in which oxygen on the surface is bound to titanium a drastic change in the shape of the 418 eV Ti peak is obtained [15].

From the surface compositions obtained and the steady state compositions the sputtering yield ratio in the Ti-N system was calculated according to equation (10). The result is shown in Fig 12. The sputter yield ratio \( S_N/S_{Ti} \) increases from 0.8 to 1.1 as the nitrogen content in the samples increases. This means that at lower nitrogen concentrations titanium is preferentially sputtered whereas nitrogen is sputtered preferentially at the highest concentrations. Films with yield ratios close to or greater than unity have all single phase \( \delta \)-TiN structure. Yield ratios lower than one is obtained from films with two phase structure of either \( e \)-Ti\(_2\)N and \( \delta \)-TiN or \( e \)-Ti\(_2\)N and \( \alpha \)-Ti. As seen from the figure, the results are compatible with a linear behaviour of the yield ratio. It is, however, more probable that there is a step in the curve, as indicated in the figure. The step should then be located at the composition where the structure abruptly changes from a two phase structure to a single phase \( \delta \)-TiN structure.

As already mentioned no effect of preferential sputtering is observed in the Ti-C system. For samples with the highest carbon concentrations (single phase TiC structure) these results are also in agreement with those obtained by Wehner [27] on TiC\(_{1.12}\) and TiC\(_{0.92}\) samples. More surprising, however, is the lack of preferential sputtering in the region where a two phase \( \alpha \)-Ti and TiC structure exists. Preferential sputtering of Ti similar to that observed in the Ti-N system would have been expected. Since the grain sizes in the Ti-C
Figure 12: Sputtering yield ratio for nitrogen and titanium calculated from equations (9) and (10) vs. nitrogen to titanium atomic ratios.
system (as measured from X-ray line broadening) are smaller than those in the Ti-N system, the interactions between the two phases are stronger, which may be the reason for the change in sputtering rate of the pure Ti phase. Such effects have also been noticed in 0/Ni cermet films [28] where a slight increase in the nickel content was found after sputtering, although bulk Ni sputters more than twice as fast as MgO.

To summarize this section, we have shown that even if it to some extent exists, preferential sputtering is not a serious problem in the system studied. The results show that the sputtering yields in compounds are not comparable to the yields from the pure elements. In the Ti-C case a yield ratio of 1.0 was obtained whereas the yield ratio with data from pure elements give a value of 0.24 for \( S_C/S_{Ti} \) [29]. To determine more accurately the effects of preferential sputtering in these systems detailed investigations with samples prepared "in situ" are needed. Except for the discrepancy in comparison with pure elements the matrix does not influence the different parameters in the expression for the relative sensitivity factors to a large extent. This is mainly due to the fact that the parameters are expressed as ratios. In the Ti-C system no variations with composition (< 1%) in any of the different ratios were found whereas in the Ti-N system a small increase in the escape depth ratio was noticed when the amount of nitrogen increased from 0 to 50 at.%. In this system, the ratios between the sputtering correction factors were found to decrease with increasing nitrogen content. However, even if this decrease is larger than the increase in escape depth ratio no deviation from linearity was noticed in the peak height plot (Fig 5).
From the peak height plots the accuracy of the measurements of $p_{rel}^S$ is estimated to be a few per cent. In order to estimate the accuracy of the composition values different determinations on identical samples were made. Spectra were recorded during different pump-downs on several different occasions. Analysing conditions such as primary electron current, modulation voltage, sensitivity and sweep rate were also varied. From these results, the total accuracy in the determination of the metalloid to metal ratio was estimated to be of the order of 5%. For the Ti-N system the accuracy for samples containing less than about 15 at. % N are somewhat worse, (10-15%). This is due to the uncertainty in the determination of the height of the positive excursion of the nitrogen peak.

4 CONCLUSIONS

It has been shown that quantitative Auger analysis can be applied both to the binary systems Ti-C and Ti-N and to the ternary Ti-C-N system. Matrix effects and their variations with composition have only minor influences on the relative sensitivity factors. For the Ti-C system no influence of preferential sputtering was noticed whereas for the Ti-N system minor changes were observed. For N/Ti ratios less than 0.8, Ti is preferentially sputtered whereas for higher ratios N is preferentially sputtered instead.

Using the method described, fairly accurate determinations of the compositions of titanium nitrides, carbides and carbonitrides may be obtained. The total accuracy of the metalloid to metal ratio in these systems can be estimated to be about 5%. One major advantage of the AES method is that small amounts of material are needed which makes the method especially suited for thin film applications.
ACKNOWLEDGEMENT

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Kinetics of Nitride Formation on Titanium Targets during Reactive Sputtering


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During reactive sputtering processes formation of surface compounds on the target leads to large reductions in deposition rate. The formation of such layers during the reactive sputtering of titanium with Ar-N$_2$ ion beams have been studied "in situ" using Auger electron spectroscopy. The kinetics of the process were studied by monitoring the AES nitrogen signal with time. The amount of nitrogen on the target surface was estimated using a simple kinetic model. The time dependence was found to be in agreement with the exponential rate predicted by the model. To explain fully the processes occurring, chemical reactions at the surface, altering e.g., the sticking probability and penetration of reactive ions into the target lattice have to be taken into account. It is also shown that the stable δ-TiN phase is formed on the target surface. The most important parameter for the formation of the nitride layer on the target is the ratio between the number of Ar and N$_2$ ions impinging. The total number of N$_2$ ions
at a fixed N₂-Ar ratio, i.e. the degree of ionization was also found to be important. The energy, however, was found to have only a minor influence on the formation of the nitride layer. The resulting nitride layers during ion beam sputtering are also compared with layers formed on the target during reactive sputtering of titanium in an ordinary r.f. sputtering apparatus.
INTRODUCTION

During the last decade there have been several papers describing the mechanism of reactive sputtering [1-12]. When sputtering a metal in a reactive gas reactions may, in principle, occur on the target surface, on the substrate surface or "en route" in the gas phase. In the pressure range and for the substrate to target distances normally used for magnetron and rf sputtering the cross-section for a gas phase reaction is negligible, so that the reactions mainly occur on the substrate and/or target surfaces. Reactions occurring at the target lead to formation of a compound on the surface. Depending on the type of reactive gas, oxide, nitride or carbide layers may for instance be formed. The presence of a surface compound (target poisoning) often leads to a large reduction in sputtering rate and hence also in deposition rate. Reductions by factors as large as 5-30 have often been observed [3-12]. Different models for the processes on the target have been proposed, e.g., for metal-oxygen systems Greiner [1,2] has put forward a simple model assuming a logarithmic oxidation law and additive oxidation and sputtering rates. A similar model but with a function including the partial pressure of oxygen has also been proposed by Heller [3]. For the titanium oxygen system, a similar model has been used by Geraghty and Donaghey [4,5]. Recently, Maniv and Westwood [6,7] studied the kinetics of target reactions during reactive sputtering of Al and In$_{0.9}$Sn$_{0.1}$ in the presence of oxygen. They studied the time dependence of the total pressure after changes in oxygen flow rate or sputtering power and attributed the changes to the formation of an oxide on the target surface. From these measurements they concluded that, at least for Al, the oxidation of the target follows a parabolic rate mode.
Models using adsorption isotherms, for example the Langmuir adsorption isotherm, to describe the fractional surface coverage of reactive gas species on the target surface have also commonly been used [8,9,11,12]. Abe and Yamashina [8] have proposed a kinetic model with a fractional surface coverage similar to that obtained from the BET adsorption isotherm [14]. This model was later modified by Shinoki and Itoh [9] to account for gettering by the sputtered metal atoms. Recently Eltoukhy et al. [11] presented a model which accounts for changes in processes occurring at the target as well as changes in discharge parameters dependent on the partial pressure of the reactive gas. This latter model uses the Langmuir adsorption isotherm.

Since processes occurring in glow discharges are of a very complex nature, it is almost impossible to make a fully quantitative description. Simplifying assumptions are needed. For example the models and descriptions presented have not taken into full account the penetration of ions into the solid lattice and the subsequent degradation of kinetic energy through collision cascades. Furthermore, essentially indirect observations of the target processes occurring have been made. No observations of the interactions and reactions occurring at target surfaces using, e.g., surface analysis techniques have as yet been presented. Not only target reactions are of importance in the study of reactive sputtering but also as mentioned above the reactions occurring at the substrate surfaces. A detailed description of processes at substrate surfaces and their influence on the structure and properties on reactively sputtered films of titanium-nitride and carbide will be presented elsewhere. This paper reports on Auger electron spectroscopy studies of reactions occurring on titanium surfaces simultaneously bombarded with ions of Ar and N₂. In this case, the target was bombarded with ions originating from an ion gun and not from a glow
discharge plasma. These measurements are also compared with measurements of the composition of titanium target surfaces exposed to different rf Ar-N\textsubscript{2} glow discharges.

2 EXPERIMENTAL DETAILS

The experiments were carried out in a commercial scanning Auger spectrometer (Varian CMA/LEED Console Fast Cycle System 981-2001) with a base pressure of 1x10\textsuperscript{-10} torr after a 24 hour bakeout. The analysis was performed using an electron beam having a kinetic energy of 3keV and a current of 2.5 \(\mu\)A. The Auger electrons were analyzed using a single pass CMA having a energy resolution of 0.25%. A modulation voltage of 2V\textsubscript{p-p} was applied to the analyser and the spectra were recorded with a 5eVs\textsuperscript{-1} scan speed.

Depth profiling was performed using ion-bombardment with argon (99.9997%) at a pressure of 5x10\textsuperscript{-5} torr and with an energy of 3keV, and a current density of 0.1 mA cm\textsuperscript{-2}. The ion gun was mounted to give a beam incidence angle of 70\textdegree, and in order to minimize possible crater effects, it was slightly rastered. These conditions gave an etch rate of about 14 nm min\textsuperscript{-1} for pure Ti samples and 4.5 nm min\textsuperscript{-1} for pure and homogeneous TiN samples. The same ion gun was also used for the mixed argon-nitrogen ion bombardment. It was then operated with accelerating potentials varying from 0.5 to 3kV and current densities varying from 3 to 115\(\mu\)A cm\textsuperscript{-2}. The high purity argon (99.9995%) and nitrogen (99.9992%) gases were introduced into the sample chamber in a dynamical flow mode by means of leak valves. All the experiments with Ar-N\textsubscript{2} mixtures were carried out at a total pressure of 5x10\textsuperscript{-5} torr as measured by a nude ionization gauge. The samples used for "targets" consisted of 0.5 \(\mu\)m thick titanium films on glass substrates. They were prepared using electron beam evaporation of high purity Ti
(99.99%) at a constant rate of 0.5 \mu m/min. The pressure during the evaporation was kept below 2\times10^{-6}\text{torr}. Using AES it was not possible to detect any impurities such as carbon or oxygen in films prepared in this manner. Before starting the experiments on these films in the Auger equipment the surface impurities as well as the surface oxide layer were eliminated by sputtering in pure argon for one minute. The results obtained "in situ" in the Auger spectrometer were compared with results obtained in an r.f. glow discharge process. To make such a comparison possible the central part of the target could be removed for analysis after each sputtering experiment. The apparatus for the r.f. sputtering experiments is described elsewhere [15]. The transportation in air of the target before analysis introduces some uncertainties into the results. They are, however, good enough for a qualitative comparison with results obtained in more simplified sputtering processes such as ion beam sputtering in the Auger spectrometer.

Auger studies of nitrogen reactions on titanium are complicated by the fact that the main Auger electron emission from nitrogen (KL_{2,3}L_{2,3} at 381 eV) occurs at an energy that overlaps the L_{3}M_{2,3}L_{2,3} transition from titanium. The changes occurring in the differentiated AES spectrum of Ti in the energy region between 320 and 460 eV when nitrogen is added are shown in Fig. 1. We have earlier [16] shown that for titanium-nitrogen compounds the amount of nitrogen can be represented by the positive excursion at 377 eV of the N KL_{2}L_{3} peak and the amount of titanium by the negative excursion of the Ti L_{3}M_{2,3}M_{4,5} peak located at 418 eV. Even if it is possible to make quantitative analysis of the Ti-N system, the results presented in this paper are only expressed as N/Ti peak height ratios.
Fig 1.
Changes in a selected portion of the differentiated AES spectrum of Ti after different exposures to nitrogen
a) Clean Ti, b) Ti exposed to 100 L of N\textsubscript{2}, c) Ti exposed to an Ar-10 percent N\textsubscript{2} ion beam of 3 keV with 6.2 \times 10^{14} ions cm\textsuperscript{-2} s\textsuperscript{-2} until steady state was reached.
RESULTS

The typical decrease in deposition rate with increasing partial pressure of the reactive gas is shown in Fig. 2 for titanium rf. sputtered in the presence of nitrogen. Also shown in the figure is the amount of nitrogen (expressed as N/Ti peak height ratio) on the target surface versus the mole fraction of nitrogen in the sputtering gas. Since the target surface was exposed to atmosphere before analysis the error limits are large, but it is clearly seen that when the deposition rate starts to decrease the nitrogen content on the target surface increases. A similar increase in the N/Ti peak height ratio with increasing amount of nitrogen is also observed when titanium surfaces are bombarded with Ar-N\textsubscript{2} ion beams. The resulting N/Ti ratios as determined by AES analysis "in situ" are shown in Fig. 3 for three different ion bombardment fluxes and energies. When the flux and energy are increased the onset of the increase in the N/Ti ratio is moved to a higher nitrogen content. This shift is understandable if the sputtering rate increases faster than the nitriding rate on the target surface. In Figs. 2 and 3 it is also observed that when the amount of nitrogen in the sputtering gas (J\textsubscript{N\textsubscript{2}}/J\textsubscript{Ar}) exceeds about 3 percent a saturation value of the N/Ti ratio is approached, this value increasing with ion bombardment flux and energy. The reason for this effect is discussed later.

To understand the formation of the nitride layers, it is important that the kinetics of the formation process are known and depth concentration profiles established.

3.1 Kinetics

The kinetics were studied by recording the change in the nitrogen peak intensity with time for different ion bombardment fluxes (see Fig. 3).
Fig. 2 Deposition rate (●) and N/Ti peak height ratio at the target surface (○) vs. percent N\textsubscript{2} in the sputtering gas. The depositions were performed in an rf glow discharge process.

Fig. 3 N/Ti peak height ratio at the target surfaces vs. percent N\textsubscript{2} in the sputtering gas. The results were obtained during ion beam sputtering "in situ". Results for three different ion energies and fluxes are shown.
The studies were carried out with a nitrogen concentration in the sputtering gas of 10 percent, which is well above the saturation value (see Fig. 3). Depending on the flux and energy the time to reach steady state varied from 8 to 70 seconds.

In order to estimate the amount of reactive gas on the target surface, \( n \), and its variation with time a simple kinetic model can be applied. For fractional surface coverages \( n < n_t \), where \( n_t \) is the total number of sites available on the target surface, the target reaction can be written as follows.

\[
\frac{dn}{dt} + \frac{n}{\tau} = k
\]

where \( J_{N_2} \) and \( J_{Ar} \) represent the impinging flux of \( N_2 \) and \( Ar \) ions respectively, \( \alpha \) the sticking probability for \( N_2 \) ions and \( S_{N_2} \) and \( S_{Ar} \) the sputtering yields for nitrogen on the titanium surface bombarded with \( N_2 \) and \( Ar \) ions respectively. This equation can be rearranged into

\[
\frac{dn}{dt} = J_{N_2} \alpha + 2(1 - \frac{n}{n_t}) - J_{N_2} S_{N_2} n - J_{Ar} S_{Ar} \frac{n}{n_t}
\]
\[ n = k_T(1-e^{-t/\tau}) \]  

(5)

As is seen from Fig. 4, there is very good agreement between the experimentally observed results and equation (5) indicating that the simple kinetic model is a good approximation. In the cases studied in this work, the number of impinging Ar ions is larger than the number of N\(_2\) ions by at least a factor of 10 and since the sputtering yield \(S_{\text{Ar}}^{\text{N}}\) is smaller than \(S_{\text{N}}^{\text{N}}\) due to the lower mass of the N\(_2\) ions, the second term \(J_{\text{N}_2}S_{\text{N}}^{\text{N}}\) in equation (3) can be neglected. The time constant for the reaction can then be written as

\[ \frac{1}{\tau} = \frac{J_{\text{N}_2}N_2}{n_t} (2\alpha + \frac{J_{\text{Ar}}S_{\text{Ar}}^{\text{Ar}}}{J_{\text{N}_2}N_2}) \]  

(6)

If \(\alpha\) and \(S_{\text{Ar}}^{\text{Ar}}\) do not vary with nitrogen flux a straight line should be obtained when \(1/\tau\) is plotted versus the impinging nitrogen flux keeping the ratio \(J_{\text{Ar}}/J_{\text{N}_2}\) constant. Fig. 5 shows such a plot. For nitrogen fluxes above \(1\times10^{13}\) ions cm\(^{-2}\)s\(^{-1}\), a reasonably linear fit is obtained. For low fluxes, a deviation is observed which probably is due to a change in \(\alpha\) with \(N_2\) ion flux. As can also be seen from Fig. 5, the variation in the time constant with energy is small. This is also expected from equation (6) since the value of \(S_{\text{Ar}}^{\text{Ar}}\) increases only slowly with energy in the range studied [17,18]. The results are in agreement with those obtained by Taylor, Lancaster and Rabalais [19-21] in studying the interaction between nitrogen ions and various materials using photo electron spectroscopy. They found that the amount of nitrogen on the surface was strongly dependent on ion dose up to a certain saturation dose and essentially independent of ion kinetic energy over the 30-3000 eV range.
Fig. 4  Nitrogen peak height vs. time of ion bombardment. The results for two different nitrogen ion fluxes are shown. The solid lines are values calculated using equation (5).

Fig. 5  Reciprocal time constant vs. nitrogen ion flux. The influence of the ion energy is seen to be small.
When steady state is reached the number of $N_2$ molecules at the surface, $n_{st}$, is obtained from equation (5)

$$n_{st} = k = \frac{J_{N_2}}{J_{Ar}} \alpha^2 = \frac{J_{N_2}}{J_{Ar}} \frac{1}{\alpha S_{N_0}^Ar} n_t$$

(7)

Defining the onset of detectable nitrogen on the surface to be the point where $n_{st} = 1$ yields the ratio $\frac{J_{N_2}}{J_{Ar}}$ at this point

$$\left( \frac{J_{N_2}}{J_{Ar}} \right)_* = \frac{S_{N_0}^Ar}{2\alpha} \frac{1}{n_{t-1}}$$

(8)

If $S_{N_0}^Ar$ increases or $\alpha$ decreases $\left( \frac{J_{N_2}}{J_{Ar}} \right)_*$ is shifted towards higher values. This is also in agreement with the results obtained, (see Fig. 3).

As discussed earlier an increase in energy implies an increase in the sputtering yield $S_{N_0}^Ar$.

In Fig. 3 it is also seen that the N/Ti peak height ratio at saturation increases when the number of impinging ions and their energy increase. It is, however, not possible to explain this using the simple kinetic model since according to the latter an increase in energy should decrease the amount of nitrogen on the target surface. It should, however, be noted that the kinetic model ignores any depth dependence of the processes occurring. Chemical reactions which can act as driving forces and for example influence the value of $\alpha$ are also ignored, and it will be shown in the following that both this and the penetration of the ions into the target play a significant role in the processes occurring.
3.2 Depth profiles

A typical depth profile of the nitride layer formed on the target surface, when it is exposed to a nitrogen-argon ion beam, is shown in Fig. 6a. In Fig. 6b a similar depth profile is shown for a surface exposed to a pure nitrogen ion beam. To facilitate comparison both distributions are normalized to the same initial value. Also shown in the figures are values calculated using a model for ion collection during sputtering [22]. In that model the atom concentration as a function of depth \( z \) is given by

\[
c(z) = (2S)^{-1} \left[ 1 - \text{erf} \left( \frac{z-R_p}{\sqrt{2}\sigma} \right) \right]
\]  

(9)

where \( S \) is the sputtering yield and \( R_p \) and \( \sigma \) are the projected range and projected range straggling respectively. The latter parameters can be calculated according to the LSS theory [23] and the approximation rules proposed by Schiøtt [24]. Treating the \( N_2^+ \) beam as two atoms each with half the original energy [20,21] the projected range was found to increase from 1.3 nm at an ion energy of 0.5 keV to 4.3 nm at 3 keV. The projected range straggling was found to be approximately equal to the projected range.

Using these results, equation (9) and the finite escape depth of the Auger electrons, the nitrogen Auger electron intensity was calculated as a function of depth and then fitted to the experimental data. The electron escape depth for nitrogen KLL Auger electrons in titanium was calculated according to Seah and Dench [25]. The calculation of the Auger electron intensity followed the same procedure as the one used by Malherbe and Hoffmann [26] when studying low energy nitrogen implantation profiles in cobalt.
From Fig. 6 it can be seen that the agreement between the results and the theoretical implantation profile is reasonable for the case where only the surface was bombarded with nitrogen ions. At the tail of the distribution, however, a deviation exists. The same tendency was observed by Malherbe and Hoffman [26]. It has been shown [21] that a nitrogen ion beam is composed approximately of 96% $N_2^+$ and 4% $N^+$ ions. Since the model only takes one type of ions into account (in this case the $N_2^+$ ions), the long tail in the measured implantation profile may be due to the fact that the $N^+$ ions penetrate deeper into the lattice than the $N_2^+$ ions. When both argon and nitrogen ions bombard the target, the deviation from the theoretical distribution is larger. It is also seen that when argon is added to the ion beam, the nitrogen penetrates deeper into the target. The N/Ti peak height ratio at the surface also increases from 0.7 to 1.3 for the case shown in Fig. 6. It is probable that besides knock-on effects there is an enhanced diffusion of nitrogen atoms caused by the ion bombardment. Low energy ion bombardment has been shown by many workers [27-30] to enhance diffusion by introducing large concentrations of point defects into the sample. It is also known that large compressive stress gradients are built up in the surface layer during ion bombardment. For example, Hartley [31] has measured biaxial compressive stresses of the order of the yield strength of the metal when steel was bombarded with argon ions at a dose of $5 \times 10^{16}$ Ar ions cm$^{-2}$. These stresses can also lead to the migration of certain species away from the surface.

The total number of nitrogen atoms entrapped in the target can be found by taking the integral over the depth distribution. In our case, we have integrated the nitrogen Auger electron intensity over depth in order to get a representation of the number of atoms entrapped, $n$, in the target. The values of $n$ have been normalized by putting the value obtained at the
Fig. 6  Normalized nitrogen Auger signal vs. depth below the surface. The solid curves represent the graph resulting from calculation of the nitrogen Auger signal using equation (8).  
a) Titanium surface bombarded with both Ar and N$_2$ ions, 
b) titanium surface bombarded with N$_2$ ions.
highest energy and highest impinging ion flux equal to one. In Fig. 7 the
values of $n$ are plotted vs. nitrogen ion flux and energy. All the values
have been obtained at a $J_{N_2}/J_{Ar}$ ratio of 0.1. Whereas only a small increase
in $n$ with ion energy is observed $n$ increases rapidly with ion bombardment
flux up to a saturation value. With the conditions used, saturation occurred
at $5 \times 10^{13}$ ions cm$^{-2}$s$^{-1}$. Below the saturation value $n$ is proportional to
$J_{N_2}^1$ as determined from a double-logarithmic plot. These results again
agree with the results of Taylor, Lancaster and Rabalais mentioned earlier
[20-22]. It should, however, be noted that the minimum ion dose required
to reach saturation in our case is about $5 \times 10^{14} N_2$ ions cm$^{-2}$, if the time
needed to reach saturation is 10s, whereas the dose needed in their case
varied from 1 to $5 \times 10^{16}$ ions cm$^{-2}$ depending on the material. Such a diffe-
rence in the saturation dose needed is also in agreement with what was
earlier mentioned about an increased reactivity and penetration when the
surface is simultaneously bombarded with $N_2$ and Ar ions.

4. DISCUSSION

The simple kinetic model presented correctly predicts many of the
obtained results but since it does not take into account any depth depen-
dence of the various parameters, some results are not explained. Whereas a
decrease in the nitrogen surface concentration with energy and ion flux is
expected according to equation (7) an increase is actually observed. To
understand this discrepancy, a discussion of what happens to an energetic
ion approaching and colliding with a surface is needed.

It has been shown [32,33] that ions approaching a surface have high
probabilities of undergoing charge exchange neutralization with the surface
in the form of resonance neutralization or Auger neutralization at distan-
ces 5-6Å from the surface. After neutralization the energetic neutrals
Fig. 7 The number of N atoms entrapped in the target, $\eta$, vs. nitrogen ion flux at constant energy. Also shown in the figure is $\eta$ vs. ion energy when the flux is constant. The values of $\eta$ have been normalized by setting the value obtained at the highest ion flux and energy, to one. All values were obtained after steady state was reached. The solid line in the $\eta$ vs. $J_{N_2}$ graph is calculated according to $\eta = 1.4 \times 10^7 (J_{N_2})^{\frac{1}{2}}$. 

$E = 3$ keV

$J_{N_2} = 0.9$ \times 10^{13}$ ions cm$^{-2}$ s$^{-1}$
collide with the surface and the probability of dissociation is high [21]. For the dissociation of $N_2$ at tungsten surfaces the activation energy for dissociation has been determined [34] to be about 9 eV. In the energy range studied in this paper, this means that the two resulting nitrogen atoms will have approximately half the original energy. These nitrogen atoms formed at the surface loose their energy in collision cascades until they are thermalized within the lattice. Once thermalized, the atoms become entrapped as neutral atoms (or molecules) in the bulk, react chemically with the bulk atoms or diffuse back to the surface. In section 3.2 it was shown that the atoms penetrate the lattice of the target and due to ion bombardment enhanced diffusion, the penetration depth is larger than that predicted by the LSS theory. It is thus probable that the diffusion of nitrogen atoms back to the surface is of minor importance in the cases studied. From Fig. 3 it can be seen that as the total ion flux and ion energy increases (the ratio $J_{N_2}/J_{Ar}$ remaining constant) the N/Ti ratio for a saturated surface increases. By taking into account other measurements not shown in Fig. 3 it is found that for larger fluxes the N/Ti surface ratio approaches a value between 1.2 and 1.3. We have earlier shown [16] that the N/Ti ratio (as defined in section 2) is 1.20±0.06 for stoichiometric δ-TiN. From Fig. 7, it was seen that the total number of nitrogen atoms entrapped in the target, $n$, increases with nitrogen ion flux up to a saturation value. If the energy is increased (at a constant ion flux), only a small increase in $n$ is noticed. The N atoms will of course penetrate to larger depths with increasing energy but this increase in penetration is compensated for by an increase in sputtering yield. It thus seems that the increase in the nitrogen/titanium ratio proceeds until the number of nitrogen atoms available is sufficient to form the stable δ-TiN phase on the target surface. The driving force for this reaction is provided by its
free energy of reaction. The fact that \( n \) was found to be proportional to \( J_{N_2}^{\frac{1}{2}} \) also supports the formation of the stable \( \delta \)-TiN phase on the target surface. Since as the concentration of titanium is kept constant on the target surface, the law of mass action [35] predicts the chemical equation to be

\[
N_2 + 2Ti \rightarrow 2TiN
\] (10)

It should also be noted that no evidence for the formation of the \( \varepsilon \)-\( Ti_2N \) phase on the target surface is found, either in the behaviour of the deposition rate or in the composition of the target surface. The existence of this phase has been discussed by Abe and Yamashina [8]. However, since this phase is not as stable as the \( \delta \)-TiN phase and stable only over a very limited composition range [36], it is doubtful if it exists on the target surface. The chemical reactions occurring on the target surface imply for instance that the sticking probability will be affected by the chemical status of the target compound to a large extent and that adsorption isotherms such as, for example, the Langmuir adsorption isotherm will not be valid. Effects of the free energy of formation on target reactions have also been discussed by other workers. For example, Eltoukhy et al. [11] studied the reactive sputtering of In in Ar-\( N_2 \) discharges, and they explained the fact that no nitride layer was formed on the target surface by the low heat of formation of InN. Castellano [12] has developed an empirical model in which the transition pressure (the pressure at which a compound is formed on the target surface and the deposition rate drops) is given by

\[
P_0 = 3.0 \times 10^{-4} \frac{R}{\Delta G^0}
\] (11)
where $R$ is the deposition rate in nm min$^{-1}$ and $\Delta G^0$ is the free energy of formation expressed in kcal mole$^{-1}$. $P_0$ is then obtained in torr. Relation (11) is only useful as a guide. In our case with rf. sputtering a value of $P_0 = 1.6 \times 10^{-4}$ torr is obtained with the use of $\Delta G^0 = \Delta H^0 = 88.1$ kcal mole$^{-1}$ [36], where $\Delta H^0$ is the heat of formation. Experimentally it is observed (see Fig. 2) that the onset of target nitriding starts at about $1 \times 10^{-5}$ torr and that the saturation value of the N/Ti peak height ratio is reached at about $1 \times 10^{-4}$ torr.

The shift of $(J_{N_2}/J_{Ar})_s$ (the value where nitrogen starts to accumulate on the target surface) towards higher values as the ion energy and flux are increased is also understandable since when only small amounts of nitrogen are collected on the target surface, no stable compound such as $\delta$-TiN will be formed. The nitrogen atoms will instead be in a state similar to a chemisorbed state or dissolved in the Ti lattice at the outermost surface. Chemisorbed nitrogen on tungsten has been shown [37] to have a very high sputtering yield almost comparable to silver when bombarded with Ar ions. It therefore seems reasonable that nitrogen is preferentially sputtered at low concentrations on titanium target surfaces. A small effect of preferential sputtering of nitrogen in homogenous $\delta$-TiN films has also been reported previously [16]. An energy increase accordingly implies a shift of $(J_{N_2}/J_{Ar})_s$ towards higher nitrogen contents in the sputtering gas. However, when the nitrogen content in the sputtering gas becomes high enough to allow nitrogen to be more strongly bound on the target surface the increase towards the saturation value will proceed faster at higher ion energies. This is also in agreement with the obtained results, (see Fig. 3).

Most of the results presented in this paper have been obtained when titanium targets were bombarded with Ar-N$_2$ ions originating from an ion
gun. In a glow discharge process the interpretation of the results is more complicated due for instance to the fact that the energy and angular impact distributions of the bombarding ions, the concentration and distribution of the electrons in the discharge, effects of the radiation from the glow discharge, etc., are not known. It can, however, be seen from Figs. 2 and 3 that the increase in nitrogen concentration with increasing nitrogen content in the sputtering gas is similar in both cases suggesting that the processes discussed above for ion beam sputtering are also valid in glow discharge sputtering.

5. CONCLUSIONS

When Ar-Np ion beams impinging on a Ti target and the amount of nitrogen ions is high enough a nitride layer is formed on the surface, the AES spectrum of which is similar to that of bulk 6-TiN. The energy of the ions in the energy range investigated (0.5-3 keV) appears to have only a minor influence on the nitride layer.

The time-dependence of the building up of the nitride layer is given by a simple exponential relation. The amount of nitrogen at the outermost surfaces is given by:

\[ n = k (1 - e^{-t/\tau}) \]  \hspace{1cm} (12)

However, for a complete explanation, the processes which occur during the penetration of the ions into the target have also to be taken into account. It was found that the depth of penetration of the nitrogen into the titanium lattice was larger than expected from LSS theory. For a mixed Ar-N2 beam, the depth was larger than that obtained using only a nitrogen beam.
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MECHANISMS OF REACTIVE SPUTTERING OF TITANIUM NITRIDE AND TITANIUM CARBIDE

I. INFLUENCE OF PROCESS PARAMETERS ON FILM COMPOSITION

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Reactive sputtering of titanium in mixed Ar-N₂ and Ar-CH₄ discharges was studied by measuring both the compositions of deposited films and of layers formed on the target. The sputtering experiments were performed in a diode rf-sputtering unit and the measurements of composition were performed using Auger electron spectroscopy. The results show that the amount of gas incorporated into the growing films depends on whether or not a compound has been formed on the target. At low pressures where no such compound is formed the incorporation of the reactive gas follows an adsorption isotherm similar to the Langmuir adsorption isotherm, with very low values of sticking probability. At higher pressures species originating from the target determine the composition of the coatings. Important process parameters were found to be the ratio between the amounts of reactive and sputtering gas, the ion current density and the voltage applied to the target.
1. INTRODUCTION

Because of their unique properties thin films of various transition metal carbides and nitrides are of high technological importance. Their extreme hardness makes them useful in increasing the wear life of steel parts such as cutting tools, punches and bearing surfaces [1-4]. Because they have both good high temperature strength and corrosion resistance, they can also be used as high temperature structural materials [5]. The nitrides also have interesting electrical properties and are therefore used in applications such as integrated circuitry [6]. In addition some of the nitrides and carbonitrides have interesting optical and superconducting properties [7-8].

Thin films of carbides and nitrides are obtained either by chemical vapour deposition (CVD) 9-10 or by some kind of reactive physical vapour deposition (PVD) method [1-4]. Due to the high reaction temperatures involved the use of the CVD process is limited to applications where the substrate and the coating-substrate interface are not damaged by the high temperature. Among the PVD methods reactive sputtering is that most frequently used. Both d.c., r.f. and magnetron sputtering are in use today, the latter method being of the greatest industrial importance due to its high deposition rates. During reactive sputtering processes, it is however, hard to maintain high deposition rates since deposition rates decrease by as much as a factor of 5 to 30 when the partial pressure exceeds a certain value (of the order of 1% of the total pressure). The reason for this decrease is that on the target surface a surface compound with lower sputtering yield than the pure metal is formed. The formation of such a layer on the target surface has been studied by a large number of workers [11-14] and we have recently presented "in situ" observations of the kinetics of nitride formation on titanium targets using Auger electron
spectroscopy [15]. The formation of a compound on the target not only leads to a reduction in deposition rate but can also influence the growth of the film itself. It has for example, been shown by Coburn et al. [16] that in certain cases the intensity of sputtered molecules may exceed that of sputtered atoms when a compound target is sputtered. The fraction of sputtered molecules depends on the bond strength between the metal and the metalloid in the compound. Molecules that impinge on a growing film will in the adatom state have a lower mobility than impinging atoms and the resulting film will have higher defect densities and smaller grains. The nature of the species sputtered from the target can also influence the composition of the resulting film since different species have different sticking probabilities, e.g., for many materials the chemisorption of atomic nitrogen is much more pronounced than that of molecular nitrogen [17]. It is thus obvious that if process parameters which change the status of the target are varied the composition, morphology and crystal structure of the deposited film may be altered. This paper reports on the influence of process parameters, such as the total pressure, the partial pressure of the reactive gas and the power applied to the target on the composition of films reactively r.f. sputtered in Ar–N$_2$ and Ar–CH$_4$ discharges.

2. EXPERIMENTAL PROCEDURE

Polycrystalline titanium targets, 15 cm in diameter, with a purity better than 99.99% were r.f. sputtered in mixed Ar–N$_2$ and Ar–CH$_4$ discharges with the concentration of the reactive gases ranging from 0 to 100%. The depositions were performed in a vacuum system equipped with a diffusion pump–baffle combination (Varian Sputtorr 175) capable of keeping a constant pumping speed of 250 l/s up to pressures as high as 15x10$^{-3}$ torr. A tita-
nium sublimation pump was also used in order to get as clean vacuum as possible. The residual gases in the system were checked using a mass-spectrometer. Before the gases were admitted into the chamber, the entire system was evacuated to a pressure of about $5 \times 10^{-7}$ torr. While the experiments were conducted at total pressures ranging from $3 \times 10^{-3}$ to $12 \times 10^{-3}$ torr the main part of the experiments was carried out at a total pressure of $5 \times 10^{-3}$ torr. The pressures were measured with an ion gauge calibrated with a capacitance manometer. Since no separately pumped mass spectrometer was used, we had no other means of controlling the partial pressure of the reactive gas than by monitoring it before and after the depositions. Since a high precision leak value was used and the pressure in the gas inlet system was kept constant, only minor fluctuations in the partial pressure (less than 5%) were noticed.

The substrates of polished steel, copper foil, fused silica and alumina were maintained at a temperature of 775 K. They were cleaned ultrasonically before evacuation and were outgassed in vacuum at a temperature of 775 K during a minimum time of 1 hour. In order to avoid alloying between titanium and copper, the copper foils were coated with 2-3 µm of nickel. The films were deposited to thicknesses ranging from 0.3 to 7 µm. The deposition rates which depend strongly on the partial pressure of the reactive gas are given for Ti-N$_2$ and Ti-CH$_4$ in Fig. 1. These values were obtained using a target to substrate distance of 4 cm and a net r.f. power at 1000W, which is equivalent to a target d.c. offset voltage of 3.6 kV and a current density of 1.6 mA cm$^{-2}$. In other experiments r.f. powers of 600 to 1400 W have been used. In all experiments, the substrates were kept at ground potential.

The composition of the films were measured using both Auger electron spectroscopy (AES) and electron microprobe analysis. The AES experiments
Fig. 1  Deposition rate vs. partial gas pressure. (●) CH₄ and (○) N₂.
were performed in a scanning Auger spectrometer (Varian 981-2001) with a base pressure of $10^{-9}$ torr. The energy analysis of the Auger electrons was performed using a single pass CMA with an energy resolution of 0.25%. The primary electron beam current used was 2.5 µA at 3 keV giving an electron beam diameter of less than 10 µm. To get rid of surface contaminants prior to analysis and to check the homogeneity of the samples, ion etching was used. The etching was performed with argon gas (99.9997%) at a pressure of $5 \times 10^{-5}$ torr and with an accelerating potential of 3 kV. The ion beam was slightly rastered to ensure a uniform current density in the area analysed. The quantification of the spectra obtained is described in detail elsewhere [18]. For the quantification of Ti-C samples the intensity ratio of the C KLL 272 eV peak to the Ti LMM 418 eV peak was used. Using these peaks a relative sensitivity factor for C to Ti of 0.95 was found. For the Ti-N case the positive part of the N KLL 380 eV peak and the negative part of the Ti LMM peak at 418 eV were used. The relative sensitivity factor in this case was found to be 1.20 for N to Ti. The compositions of a few samples were also measured using an electron microprobe connected to a scanning electron microscope (Cambridge Stereo Scan 180). In this case the concentrations of carbon and nitrogen were calculated as differences using a correction programme LINK ZAF-4. Since the probe depth is about 3-5 µm when an accelerating potential of 20 kV is used, only films thicker than this were analysed. The results of these analysis were in very good agreement with those of the AES analysis. In this paper only the results obtained by the quantitative AES analysis are presented.

Film thicknesses were measured both by examining cross-sections in the SEM and by measuring step height using a Talysurf or for the thinnest films, an interference microscope.
Crystallographic structure was determined using X-ray diffraction. The diffraction patterns being recorded with a Guinier camera using filtered CuKα1,2 radiation.

3. RESULTS

The obtained variations in film composition with the partial pressure of the reactive gas are shown for the Ti-N2 and Ti-CH4 cases in Fig. 2. The total pressure, substrate temperature and r.f. net power used were kept constant. As can be seen from this figure there are two main differences between the two cases. First of all, the reactivity is higher for the Ti-N2 case, resulting in a higher concentration of nitrogen in films made at lower partial pressures. Secondly, it is seen that whereas the nitrogen concentration increases rapidly to a value of slightly less than 50 at.% at 10^-4 torr after which it only increases very slowly, the carbon concentration increases rapidly towards 100% as soon as the partial pressure of CH4 exceeds 10^-3 torr. The latter increase is due to a direct deposition of carbon from the plasma, resulting in a carbon film on both the substrate and target surfaces. This effect is also utilized in the preparation of diamond like, or i-carbon films [19, 20]. At partial pressures somewhat below 10^-3 torr, a plateau at a carbon concentration around 50 at.% exists. It is only in this region that single-phase TiC coatings are obtained. TiC coatings can thus only be prepared in a very narrow range of CH4 partial pressures.

The effects of different total pressures on the composition of the films have also been investigated. These studies were performed for the Ti-N2 system using two different N2 partial pressures, 1x10^-4 torr and 2.5x10^-4 torr. The results are shown in Fig. 3. As can be seen, no noti-
Fig. 2 Composition of deposited films vs. the partial pressure of reactive gas a) carbon concentration vs. partial pressure of CH₄ b) nitrogen concentration vs. partial pressure of N₂.
ceable effect on the film composition is observed for $P_{N_2} = 2.5 \times 10^{-4}$ torr. For the lower $N_2$ partial pressure of $1 \times 10^{-4}$ torr, however, the N/Ti ratio decreases as the total pressure increases. In Fig. 4 these results are replotted to show the N/Ti ratio versus the mole percent of nitrogen in the sputtering gas. In the latter figure some other results (shown in Fig. 2) are also included. It is seen that the N/Ti ratio only shows a minor increase above 2 mole percent of nitrogen. Below this value, the N/Ti ratio drops rapidly and although the drop rate varies somewhat its onset is independent of the total pressure used. If the net power applied to the plasma is changed, both the dc offset voltage on the target and the current density in the plasma will change. Both these parameters have previously been shown to affect reactions occurring on the target surface [15]. A change in net power from 600 to 1400 W is equivalent to a change in target voltage from 2.2 to 3.9 kV and in current density from 1.5 to 2.0 mA/cm$^2$.

Fig. 5 shows the variation in film composition with power used for the same two partial pressures of $N_2$ discussed above. At the higher partial pressure $2.5 \times 10^{-4}$ torr, no variation with power was noticed but at the lower nitrogen pressure the N/Ti ratio decreases from 0.93 at 600 and 800 W to 0.47 at 1400 W. The reason for this is discussed below. The compositions of the target surfaces versus the partial pressure of the reactive gas is shown in Fig. 6. These compositions could be determined since the central part of the target could be removed for AES analysis after each sputtering experiment. The target compositions are expressed as N/Ti and C/Ti Auger peak height ratios instead of as compositions in atomic percent. This is done since the layers formed on the target surfaces are too thin to make accurate analysis possible. The ratios approximate the relative compositions since the relative sensitivity factors are, as already mentioned, close to one. However, the transport of the target in air before
Fig. 3  Nitrogen to titanium ratio in the deposited films vs. total pressure. Results are shown for two different nitrogen partial pressures (•) $2.5 \times 10^{-4}$ torr and (ο) $1 \times 10^{-4}$ torr.

Fig. 4  Nitrogen to titanium ratio in deposited films vs. mole percent nitrogen in the sputtering gas.
Fig. 5 Nitrogen to titanium ratio in deposited films vs. power applied to the plasma. Results are shown for two different partial pressures (●) $2.5 \times 10^{-4}$ torr and (○) $1 \times 10^{-4}$ torr.

Fig. 6 Composition of the target surface vs. partial pressure of the reactive gas. The compositions are expressed as N/Ti (○) and C/Ti (●) Auger peak height ratios.
analysis introduces some uncertainties and results in a large scatter in the data points giving, as can be seen from the figure, large error limits. The previously mentioned deposition of carbon on the target surface when the partial pressure of methane exceeds a certain value is also clearly seen in the figure. The reactions occurring on the target surface during ion bombardment have for the titanium-nitrogen case previously been described in detail [15]. In these studies, which were made in situ in the Auger spectrometer, we showed that the stable δ-TiN phase is formed on the surface and that this reaction is enhanced due to the penetration of ions into the target surface.

Since the incorporation rate of gases into the growing films depends among other parameters on the adsorption process occurring on the metal surface (21, 22), it is of course essential that the nature of this process is known. In view of this, we have in this work also studied the chemisorption of nitrogen and methane on clean polycrystalline titanium "in situ" in the Auger spectrometer. For nitrogen on titanium the amount of nitrogen adsorbed increases up to an exposure of about 8 L being thereafter constant. The results were found to be independent of whether or not the primary electron beam used for the Auger analysis, was incident on the surface during the adsorption. The amount adsorbed was also independent of whether a given surface coverage was attained with a single larger exposure or a series of successive shorter exposures. The results are in good agreement with results for Ti(0001) surfaces obtained by Shih et al. [23, 24]. By using LEED studies and observations of the behaviour of the low energy Ti-N cross-transition peak appearing at 23 eV, they were able to conclude that before the nitrogen content on the surface saturated at about 8 L a nitrogen underlayer with a structure similar to that of δ-TiN is formed at about 4L of exposure. Since a maximum in the intensity of
the cross-transition peak is observed in our work at around 2L, it seems that an underlayer is also formed on polycrystalline titanium samples. It can thus be concluded that the nitrogen molecule dissociates easily on the titanium surface without any need of ionizing radiation. Since both under- and overlayers are formed, the sticking probability is initially high since a Ti(0001) surface has $1.3 \times 10^{15}$ atoms cm$^{-2}$ and 8L of exposure corresponds to $6 \times 10^{15}$ atoms cm$^{-2}$.

For the adsorption of methane on titanium a much lower reactivity compared to nitrogen is found. Even after an exposure of 1000L only a small carbon peak corresponding to about 5% of the N peak after 8L exposure is observed. The results are, however, not independent of whether or not the primary electron beam was on during adsorption. With the beam on continuously, the amount of carbon was found to be higher than in the case when the beam was turned on only during analysis. After an exposure of $10^4$L ten times more carbon was found in the first case. This indicates that the adsorption rate of methane on titanium is considerably increased by the availability of an electron beam, which probably increases the dissociation rate of methane present.

4. DISCUSSION

To be able to control the formation of reactively-sputtered films the incidence rate and nature of the atoms and molecules arriving must be known. Also, their interactions both with one another and with the substrate surface must be known.

The rate of incorporation of material into a growing film can be expressed as the difference between the condensation rate and the re-emission rate. If resputtering and thermal desorption are considered as the reemission processes the incorporation rate of component n can be written as:
where $F_t$ is the flux of atoms or ions originating from the target, $F_g$ the flux originating from the sputtering and residual gases, $F_s$ the resputtering flux from the substrate and $\mu$ is the rate of reevaporation. Sputtering from the chamber walls also contributes to the flux of material impinging. However, if as in our case, the area of the anode is much larger than that of the cathode sputtering from the walls will be small and can be neglected. If as in this work, the substrates are kept at ground potential the growing film will only be exposed to a very small ion bombardment flux and hence the resputtering flux can be put equal to zero. If the temperature is low, the reevaporation rate $\mu$ can also be put equal to zero to a first approximation. This may be a rather crude approximation in our case since the substrate temperature used is as high as 775 K. In the following discussion, the incorporation rate $K_n$ is approximated with the first two terms in equation (1).

The flux of atoms leaving the target can be expressed as $J_n S_n$ where $J_n$ is the flux of ions bombarding the target, $S_n$ the sputtering yield of component $n$ on the target surface and $c_n$ the surface coverage of component $n$. The flux of atoms incorporated in the growing film originating from the target is then obtained by multiplying this expression by the probability, $\beta$, that an atom sputtered at the target reaches the substrate and by the sticking probability at the substrate surface, $a_{nt}$ i.e.,

$$ (F_t)_n = \beta a_{nt} J_n S_n c_n $$

The flux from the sputtering gas can be expressed using kinetic gas theory. This expression has of course also to be multiplied by the sticking probabilities of these species on the substrate surface, $a_{ng}$. Thus,
\[ (F_g)_n = a_{ng}^S \cdot k P_n \cdot X \]  \hspace{1cm} (3)

where \( k = 3.5 \times 10^{22} (MT)^{-1/2} \text{ cm}^{-2} \text{s}^{-1} \text{torr}^{-1} \), \( M \) is the molecular weight and \( T \) the temperature of the gas. The number of atoms of component \( n \) in the molecule is given by \( X \). The rate of incorporation of component \( n \) into the growing film is thus given by the sum of Eqns. (2) and (3). In our case where titanium is sputtered in either nitrogen or methane, the ratio between the nitrogen or carbon and the titanium concentration on the substrate is given by,

\[ \frac{C_n}{C_{Ti}} = \frac{a_{ng}^S \cdot X \cdot k \cdot P_n}{\beta a_{nt}^S \cdot t \cdot Ti^{0} \cdot Ti} + \frac{a_{nt}^S \cdot S \cdot t^{t}}{\alpha a_{nt}^S \cdot t^{t} \cdot Ti^{0} \cdot Ti} \]  \hspace{1cm} (4)

where \( n \) is either nitrogen or carbon. At a gas temperature of 300K, \( k \) is \( 3.8 \times 10^{20} \text{ cm}^{-2} \text{s}^{-1} \text{torr}^{-1} \) if the reactive gas is nitrogen and \( 5.1 \times 10^{20} \text{ cm}^{-2} \text{s}^{-1} \text{torr}^{-1} \) for methane. It is thus seen that to be able to explain the behaviour of the film composition as a function of, e.g., the partial pressure of the reactive gas, it is necessary to understand the chemisorption processes occurring both at the substrate surface and at the target surfaces. From the measurements of target composition (see Fig. 6), it is seen that below a certain critical pressure no reactive gas atoms are present on the target surface. This implies that at pressures lower than this critical value, only the first term in equation (4) is of importance. The composition of the growing films is apart from the sputtering of the pure element from the target, mainly governed by the direct impingement of species from the gas. At higher pressures no term in (4) is neglig-
ible and the impingement of nitrogen or carbon originating from the target is also important. In both cases, species reflected at the target surface and then reaching the substrate may also contribute. For low pressures of reactive gas, the first term in equation (4) gives the concentration of element n in the growing film

\[ C_n = \frac{\alpha_{ng}^S \cdot X \cdot k \cdot P_n}{\alpha_{ng}^S \cdot X \cdot k \cdot P_n + \beta_{Ti}^S \cdot J_{Ti}^S} \]  

(5)

An expression similar to the Langmuir adsorption isotherm is thus obtained. Since the amount of nitrogen or carbon incorporated at these pressures is small (< 5 at.%), \( \beta_{Ti}^S \cdot J_{Ti}^S \) can be approximated as the total measured deposition rate expressed in atoms cm\(^{-2}\)s\(^{-1}\). Since the amounts of nitrogen or carbon incorporated at different pressures are measured by AES, the sticking probabilities, \( \alpha_{ng}^S \), can be calculated from (5). If \( \alpha_{ng}^S \) is plotted versus inverse pressure, a linear behaviour should be obtained.

For the case of Ti-CH\(_4\), no reaction occurs on the target at pressures below 7x10\(^{-6}\) torr (see Fig. 6) which implies that \( \alpha_{NG}^S \) can be calculated for pressures lower than this value. For nitrogen only a pressure of 5x10\(^{-6}\) torr is low enough for no reaction to occur. The value of \( \alpha_{NG}^S \) will, however, be very uncertain since it is very difficult to measure small amounts (< 5 at.%) of nitrogen in titanium with AES [18]. The results for the Ti-CH\(_4\) case are given in Fig. 7 where \( \alpha_{CG}^S \) is plotted versus the inverse partial pressure of methane. It is seen that a straight line is obtained indicating a good validity of equation (5). It should be noted that the values of \( \alpha_{CG}^S \) are small. A low reactivity was also found from the chemisorption experiments that were performed in the Auger spectrometer. The reactivity is difficult to determine since the electron beam impinging on
Fig. 7  Carbon sticking coefficient $\alpha_{CG}$ vs. inverse methane partial pressure.
the surface during analysis influences the adsorption rate, the amount of carbon adsorbed increased when the electron beam was on during the adsorption. During sputtering a grounded substrate is bombarded by a large flux of energetic electrons. However, in spite of this, low values of sticking probability were obtained. Low values of reactivity between methane and various transition metals at elevated temperatures in a non-plasma environment have also been found. For example, for the temperature range 1400-2200K Hörz et al. [25] found reaction probabilities between $10^{-5}$ and $10^{-3}$. A low value of reactivity between titanium and methane has also been noticed when operating a titanium sublimation pump [26].

A small value of the sticking probability was also obtained for the Ti-N$_2$ case. A value of 0.06±0.05 was obtained at a partial pressure of nitrogen of 5x10^{-6} torr. The chemisorption studies, however, indicate a high sticking probability. The sorption of nitrogen at room temperature titanium films prepared by evaporation from a titanium filament has been studied by Harra and Hayward [27]. They showed that the sticking coefficient can vary from 0.12 to 0.85 at low nitrogen coverages, depending on the thickness of the deposited film. The increase in reactivity with thickness was explained to be due to an increase in the available surface area. The low values of sticking probability obtained in our case during sputtering may be due to the fact that thermal desorption has not been taken into account in the above discussion. If this is the case, a decrease in substrate temperature should lead to an increase in the amount of reactive gas incorporated at these low partial pressures. However, because of difficulties in maintaining sufficiently low temperatures during r.f. sputtering no such experiments have been performed. Another reason for the low sticking probability may be that the nitrogen initially adsorbed is segregated to the outermost surface during the deposition, thus reducing the number of sites available for adsorption.
When the partial pressure of reactive gas becomes high enough, a reaction starts at the target surface. Since we have shown above that the reactivity is low for methane and nitrogen impinging directly from the gas on to the growing film this contribution to the incorporation rate is neglected in the following. Equation (4) can then be rewritten as;

\[
\frac{C_n}{C_{Ti}} = \frac{a_{nt}}{a_{Ti}} \frac{S_n}{S_{Ti}} \frac{t_n}{t_{Ti}}
\]

It has earlier been shown that the ratio between the sputtering yields for carbon and titanium in homogeneous Ti-C samples of different composition is equal to 1.0 [18, 28] while it for nitrogen-titanium increases from 0.8 to 1.1 as the amount of nitrogen in the samples increases [18]. Setting \( S_n / S_{Ti} = 1 \), \( a_{nt} / a_{Ti} = (C_n / C_{Ti}) / (t_n / t_{Ti}) \) can be calculated from the measured values of film composition and the corresponding values of target surface composition. The results for different film compositions are shown in Fig. 8. As can be seen the error limits are very large for the values obtained at low concentrations, this being due to the large uncertainties in \( t_n / t_{Ti} \) when small amounts of reactive gas are adsorbed on the target. It should also be pointed out that since Auger peak height ratios are used, no correct absolute values are obtained since sensitivity factors and escape depths have been neglected. It is seen from the figure that only small variations with pressure are obtained. For both the Ti-C and Ti-N cases, a weak tendency to a decrease in sticking probability with increasing amounts of incorporated nitrogen and carbon is found. This can be due to that, the values of the sticking coefficient decrease or, to the assumption that the contribution from direct impingement of reactive gas species can be neglected, is not fully valid. It can, however, be concluded that the contribution of species originating from the target is of great importance for the composition of the films obtained.
Fig. 8  Ratio between film and target compositions vs. composition of the deposited films. The target composition ratio $\varepsilon^T_n/\varepsilon^T_{T_i}$ is set equal to the Auger peak height ratios obtained from the target after deposition. The error limits are maximum and minimum values obtained from the estimated errors.
Using mass spectroscopy Shinoki and Itoh (12, 13) have shown that during reactive sputtering of nitrides (including TiN) the ions N\(^+\), N\(_2\)\(^+\) and MeN\(^+\) were almost undetectable below a certain critical pressure. The amount of metal, N\(^+\) and N\(_2\)\(^+\) ions present above this critical pressure is about one order-of-magnitude larger than that of MeN\(^+\). These results show that titanium nitride is to a large extent sputtered as Ti and N atoms or ions. Since atomic nitrogen is known [21] to be very reactive, these measurements explain our results that a higher reactivity is obtained when species originating from the target contribute to the flux impinging on the growing film.

We have earlier studied the process of formation of nitride layers on the target during reactive sputtering of titanium in nitrogen [15]. The results showed that the pressure where a nitride layer starts to form on the target is shifted towards higher values when the energy and total ion-flux increase and that the saturation value of the N/Ti ratio reached at high nitrogen pressures (see Fig. 6) increases until it reaches a value corresponding to the \(\delta\)-TiN phase. These results are also in agreement with these obtained in this work since as is seen in Fig. 5, the nitrogen content in films sputtered at a nitrogen partial pressure of 1x10\(^{-4}\)torr decreases when the power increases. A power increase implies an increase in both target offset voltage and in current density and since 1x10\(^{-4}\) torr is on the border line to the saturation region an increase in power lowers the amount of nitrogen on the target surface and hence also in the growing films. For films sputtered at 2.5x10\(^{-4}\)torr, i.e., in the saturation region, a power increase does not affect the composition of the target and hence not either of the deposited films.
CONCLUSIONS

During the reactive sputtering of titanium in methane or nitrogen it has been shown that the amount of gas incorporated into the growing films depend on whether or not a compound is formed on the target. At low pressures where no such compound is formed the incorporation follows an adsorption isotherm similar to the Langmuir adsorption isotherm. Low values of sticking probability are, however, obtained. For high partial pressures where a compound is formed on the target the composition of the film is determined mainly by species originating directly from the target. Consequently process parameters that affect the status of the target surface also influence the composition of the resulting film. The important process parameters are the ratio between the amounts of reactive and sputtering gas, ion current density and the voltage applied to the target.
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Titanium has been reactively r.f. sputtered in mixed Ar-N\textsubscript{2} and Ar-CH\textsubscript{4} discharges on to substrates held at 775 K. The films obtained have been characterized by scanning electron microscopy, X-ray diffraction and through measurements of the microhardness and electrical resistivity. The composition of the films has been determined using Auger electron spectroscopy. The measurements show that the morphology of the deposits to a large extent influences the obtained properties of the films. For TiN coatings the electrical resistivity reaches the bulk resistivity only if coatings with full density are obtained. An observed difference in the lattice parameter for TiN thin films and bulk samples is explained using a grain boundary relaxation model. It is also shown that the heat of formation of the compounds plays an important role in the formation of carbide and nitride films. A high value promotes the development of large grains and dense structures.
1. INTRODUCTION

Part I of this work [1] dealt with the effects of different process parameters on the composition of films obtained by reactive sputtering of titanium in mixed Ar-N$_2$ and Ar-CH$_4$ r.f. discharges. Through measurements of the composition of both the target surface and the films formed, it was shown that species originating from the target determine to a large extent the composition of the growing film. The flux of species from a target during e.g. reactive sputtering is composed of metal atoms, atoms of the reactive gas and of molecules of the compound formed at the target surface [2, 3]. Since molecules both have lower symmetries and lower surface mobilities than single atoms, the growth and hence the resulting structure of the films formed is influenced. Thus, depending on the conditions under which the films are prepared, there can be large variations, in e.g., crystal structure, morphology and electrical and mechanical properties even if the composition is the same. For TiN essentially free of impurities, variations in the lattice parameter from 4.23 to 4.26 Å have been found [5-8] and for the electrical resistivity, values from 250 to 25 μΩ·cm have been reported [8-10]. For the same material, Vickers hardness values between 800 and 2500 are reported in the literature [11-17]. Even though bulk titanium nitride and carbide have the same crystal structure (B1) and only a small difference in lattice parameters (4.24 Å and 4.33 Å respectively) [18], there are large differences in the structures of thin films of these materials. For example the grain size of films grown under identical conditions is found to be smaller for carbides [16, 19, 20].

In this paper we report the effects of different process parameters during reactive r.f. sputtering on the morphology and crystallographic structure of titanium-nitride and -carbide films of different compositions. Electrical resistivity and hardness values of the films obtained are also reported and discussed.
2. EXPERIMENTAL

Polycrystalline titanium targets 15 cm in diameter with a purity higher than 99.99% were r.f. sputtered in mixed Ar-N$_2$ and Ar-CH$_4$ discharges with the concentration of the reactive gas ranging from 0 to 100%. Some experiments were also carried out with the reactive gas consisting of mixtures of N$_2$ and CH$_4$ in order to achieve films of titanium carbonitrides. A detailed description of the sputtering system is given elsewhere [1].

The substrates of polished steel, copper-foil, fused silica and alumina were maintained at a temperature of 775 K during the depositions. Before the depositions the substrates were ultrasonically cleaned in trichloroethylene, acetone and alcohol and then outgassed in vacuum at 775 K for a minimum time of one hour. To avoid alloying between the titanium and the copper the copper foils were coated with 2-5 μm of nickel. The thicknesses of the films deposited ranged from 0.3 to 7 μm. They were measured both by examining cross sections in a scanning electron microscope (Cambridge stereo scan 180) and by measuring step heights using a Talysurf 4. For the thinnest films the step heights were also measured using an interference microscope. By combining these film thickness measurements with weight gain measurements, the densities of the deposited coatings were also determined.

The compositions of the deposited films were determined using Auger electron spectroscopy (AES). A detailed description of the quantitative procedure used is given elsewhere [21]. An accuracy of 5% was obtained except for samples consisting of titanium with small amounts of nitrogen (< 10 at.%). In these cases, the accuracy was estimated to be about 15%.

The morphology of the deposits was studied using a scanning electron microscope. Both surfaces and cross sections were studied. X-ray diffraction was used to study the crystallographic structure of the films. The
diffraction patterns were recorded with a Guinier camera using filtered \( \text{CuK}_{\alpha_2} \) radiation. The \( \text{CuK}_{\alpha_2} \) contribution to the diffraction peak was separated graphically and the diffraction peaks were also corrected for instrumental broadening [22]. Both as deposited and free standing films have been analysed. In the latter case, the substrate was dissolved in nitric acid.

The electrical resistivity was measured using a standard four point probe method. The temperature coefficient was measured by recording the change in resistivity when the temperature was lowered from room temperature to liquid nitrogen temperature.

The microhardness of the films was measured on films prepared on both steel and fused silica substrates in an optical microscope (Carl Zeiss Jena Neophot 2) with a Vickers indenter. The reliability of the measurements was established by making measurements at different loads and by making a large number of indentations. The results presented are mean values of indentations made at a load of 10 g.

3. RESULTS

3.1 Morphology

Scanning electron micrographs of cross sections of typical samples containing different amounts of nitrogen and carbon are shown in Figs. 1 and 2. For the nitrogen case it is observed that samples containing small amounts of nitrogen have a relatively dense and homogeneous structure, similar to the zone 2 structure defined by Thornton [23, 24]. This is also expected, since the homologous deposition temperature \( T/T_m \) (\( T_m = \) melting temperature) was 0.37 and the total pressure during deposition was kept at 5 mtorr. When the nitrogen content in the films increases the
Fig. 1  Scanning electron micrographs showing cross-sections of different Ti-N films:

A) N/Ti ≈ 0.01  
B) N/Ti = 0.20  
C) N/Ti = 0.33  
D) N/Ti = 0.88  
E) N/Ti = 0.98  
F) N/Ti = 1.03
structure changes and becomes more open, with crystals which are separated by voided boundaries, a typical zone 1 structure (see Fig 1c). The maximum distortion of the structure is reached at a nitrogen concentration of between 20 and 30 at.%. As the nitrogen content increases further, the voided boundaries gradually disappear. When the colour of the coatings changes from grey or metallic lustre to yellow, at about 40 at.% nitrogen, the structure of the coatings becomes dense with small fibrous crystals typical of a zone T or low temperature zone 2 structures. As δ-TiN has a melting point as high as 3220 K [18] the homologous temperature is only 0.24, and a zone T structure is accordingly expected.

For the carbon case, (see Fig. 2), a dense zone 2 structure is obtained up to concentrations of about 10 at.%. Above this concentration a more open structure gradually develops and at a carbon concentration of about 50 at.% a zone 1 or low-temperature zone T structure is obtained. The melting temperature of TiC is 3340 K and $T/T_m$ thus equals 0.23.

Measurements of the densities of deposited films confirm the changes in morphology seen in the scanning electron microscope pictures. Fig. 3 shows the densities of deposited films as a function of composition. For the Ti-N case with low nitrogen concentrations the density is slightly lower than that for bulk Ti. As the nitrogen concentration increases, the density decreases and reaches a minimum at 25 at.% nitrogen. Above this concentration, it increases again and approaches the value of bulk δ-TiN. Above 50 at.% nitrogen, a rapid decrease in density is noted. The δ-TiN phase is known to be able to accomodate a large number of vacancies and it has been shown that at substoichiometric compositions the nitrogen sublattice is defective while at hyperstoichiometric compositions the titanium sublattice is defective. The theoretical lines drawn by assuming nitrogen and titanium vacancies below and above N/Ti = 1 are also plotted
Fig. 2  Scanning electron micrographs showing cross-sections of different TiC films
A) C/Ti < 0.01  B) C/Ti = 0.10  C) C/Ti = 0.43
D) C/Ti = 1.0
in Fig. 3. As can be seen, the fit to these lines is good only in a very narrow range around the stoichiometric composition. The deviations for lower or higher compositions can be explained by the development of a more open voided structure (see Fig 1d-f).

For the Ti-C case the density decreases gradually as the carbon content increases and at a carbon concentration of 50 at.% a value of 3.5 gcm\(^{-3}\) is obtained. The bulk value of the TiC phase is 4.9 gcm\(^{-3}\). The difference between these values is due to the open voided structure of the coatings. Similar low density TiC films prepared by reactive sputtering in methane have been reported by Ritchie [25]. At a C/Ti ratio of 0.75, a density of 3.63 gcm\(^{-3}\) was found and it was explained to be due to the porosity of the films. The films were found to consist of small TiC\(_x\) grains embedded in a porous matrix of carbon, where x has of course to be less than one.

3.2 Crystallographic structure

In this section measurements of interplanar spacings and relative intensities of X-ray diffraction lines for different carbon or/and nitrogen concentrations are presented. Grain sizes as obtained from X-ray line broadening are also discussed.

3.2.1 Titanium-carbon films

The relative intensities of the diffraction peaks are shown in Fig. 4 as a function of carbon concentration in the films up to 50 at.% carbon. Fig. 5 shows the crystallographic phases observed and the changes in the interplanar spacings between the lattice planes of the most intense X-ray diffraction lines as a function of composition. For pure titanium films
Fig. 3  Film density versus concentration of nitrogen (•) and carbon (○)
Also shown are bulk densities for Ti, TiN and TiC. The dashed lines
represent the theoretical density of TiN if lack of nitrogen or
titanium respectively is compensated for by vacancies in the TiN
structure.
Fig. 4  Measured relative intensities of the observed X-ray diffraction lines in Ti-C films as function of carbon concentration. The intensities have been normalized by setting the most intense line in each film equal to 100. Bulk values for Ti and TiC are also shown.
Fig. 5 Measured interplanar spacings for Ti-C films versus carbon concentration for films deposited at 775 K, 1000 W and $P_{\text{Tot}} = 5 \times 10^{-3}$ torr. Also shown are the observed crystallographic structures and bulk values of the interplanar spacings.
the structure is h.c.p. and the interplanar spacings are slightly larger than those of bulk Ti. The relative intensities of the (110) and (012) diffraction lines are somewhat higher than those for bulk material. This may be an effect of preferential growth during deposition. If small amounts of carbon are now added to the structure, a decrease in all interplanar spacings is observed and a minimum (0.3% lower than the initial value) is reached for about 3 at.% carbon. At this composition lines from the TiC phase start to appear, and the Ti interplanar spacings approach the bulk values as the carbon content is further increased. At the same concentration as that at which the minima in the interplanar spacings occur, the relative intensities of the (012) and (002) lines also have minima whereas the intensity of the (110) line reaches a maximum. Even if wide variations have been reported [26] the solubility for carbon in titanium is low. However, if the carbon was dissolved interstitially in the Ti lattice at compositions below 3 at.%, an increase in the Ti interplanar spacings should have been observed in our case [27]. However, since a decrease is actually observed it is more probable that the carbon is accumulated at the grain boundaries. Elements such as oxygen, nitrogen or carbon segregated to the grain boundaries cause compressive stresses in thin films [28]. Thus, at low concentrations of carbon, it seems as if the carbon is pushed out to the grain boundaries during growth. A similar phenomenon has also been observed to occur during the growth of co-evaporated Ni-Al films with small amounts of aluminium [29].

When the TiC phase starts to develop, the stresses in the Ti phase decrease since the carbon will now be located in the TiC phase. Between 3 and 30 at.% carbon a two phase structure of α-Ti and TiC exists. This is in accordance with the equilibrium phase diagram [26]. However, the lattice parameters of the TiC phase in the two phase region are larger than those
of the bulk reported by Ehrlich [27]. For a carbon concentration of 20 at.% he reports a value of 4.276, whereas we obtained a value of 4.308. For concentrations higher than 30 at.% carbon, a single-phase TiC structure exists. The lattice parameter for this phase, calculated from the interplanar spacings, is shown in Fig. 6. As is seen the values are within the scatter of reported bulk-data [26]. Films consisting of single phase TiC have a preferred orientation of the (111) plane (see Fig. 4), as has also been reported previously for thin films of TiC grown by physical vapour deposition [7, 19].

For small grain sizes it has been shown that the sizes determined from X-ray line broadening are in good agreement with those obtained from transmission electron microscopy [29]. For the TiC phase the grain sizes calculated from X-ray line broadening are fairly constant at about 100 nm in the two phase region. However, when single phase TiC is formed, the grain size slowly decreases and approaches a value of slightly less than 20 nm at carbon concentrations higher than 47 at.%.  

3.2.2 Titanium-nitrogen films

The interplanar spacings and the relative intensities of the most intense X-ray lines are shown versus the concentration of nitrogen in the films in Figs. 7 and 8. For nitrogen concentrations below 15 at.% only a single phase α-Ti structure has been observed and the lattice spacings increase as the nitrogen content increases. This is in accordance with what has been observed for bulk samples [27, 30]. The nitrogen atoms occupy the interstitial octahedral sites in the α-Ti lattice and thus cause an expansion of the lattice. As compared to the (011) reflection, the intensities of the (110) and (012) reflections are much higher than for bulk titanium. Above 15 at.% nitrogen reflections from the tetragonal ε-Ti₂N phase start to appear. This phase only exists as a single
Fig. 6  Lattice parameter versus composition for TiC films. The shaded area represents reported bulk values [26].
Measured relative intensities of the most intense X-ray diffraction lines in Ti-N films as a function of nitrogen concentration. The intensities have been normalized by setting the most intense line in each film to 100. In the region $\frac{N}{Ti} < 0.54$ lines originating from the (200) and (210) planes of Ti$_2$N have also been observed but are not included in the figure. Bulk values for $\alpha$-Ti and $\delta$-TiN are also shown.
Fig. 8  Measured interplanar spacings versus nitrogen concentrations for Ti-N films deposited at 775 K, 1000 W and $P_{\text{tot}} = 5 \times 10^{-3}$ torr. Also shown are the observed crystallographic structures and bulk values of the interplanar spacings.
phase in a very narrow composition range about 33 at.% nitrogen. From Fig. 8, it is also seen that values of the lattice spacings for this phase degrease when the nitrogen content increases. For the (111) and (210) planes a large expansion of the spacings is obtained for the lowest concentrations while a compression is observed at the highest nitrogen concentration.

At nitrogen concentration above 30 at.%, reflections from the δ-TiN phase starts to appear and above 35 at.% δ-TiN exists as a single phase. From Fig. 7 it is seen that the intensities of the reflections observed are close to those of the bulk in a narrow range around the stoichiometric composition. For both sub- and hyperstoichiometric compositions increases in the (111) and (220) relative intensities are observed. The interplanar spacings are seen to increase with the nitrogen content up to a maximum at a nitrogen concentration slightly less than 50 at.%. The lattice parameter calculated from the interplanar spacings for different compositions is plotted in Fig. 9 together with results for bulk samples taken from Refs. [18, 27, 30, 31]. Whereas good agreement with the bulk data is obtained for $N_{\text{Ti}} < 0.9$ and $N_{\text{Ti}} > 1.02$ larger lattice parameters are obtained in the intermediate composition region. Instead of the bulk value, 4.24 Å, a lattice parameter of 4.25 Å is found. Such a value is also commonly reported in the literature for thin TiN Films [4-9]. The explanations that have been proposed of this difference include (i) a difference in thermal expansion between the coating and the substrate (ii) the presence of oxygen and carbon impurities and (iii) the incorporation of argon during growth. Since we have measured both on films on the substrate and on free standing films with the substrate dissolved without finding any significant difference, explanation (i) can be rejected. Since depositions have been performed in mixed Ar-N$_2$-CH$_4$ discharges the effect of carbon impurities has also been investigated in this work. The
Fig. 9 Lattice parameter versus composition of 6-TiN films. The shaded area represents reported bulk values [18, 27, 30, 31].
variation in the lattice parameter with carbon-nitrogen concentration in the films is shown in Fig. 10., together with data from Refs. [32-34]. It is seen that, except for pure TiN samples, there are good agreement with earlier published bulk results. Thus it does not seem probable that the high value of the lattice parameter is due to the incorporation of carbon in the lattice. Since the nitrogen atom is larger compared to the oxygen atom [35] a contamination with oxygen should not lead to an expansion of the lattice. Incorporation of oxygen at the grain boundaries should neither lead to an expansion of the lattice [28].

Incorporation of argon in films during growth can lead to an expansion of the lattice ever if many studies [38, 39] have shown that compressive stresses occur when argon is incorporated. No indications of an incorporation of argon were noticed during the AES analysis. However, since we used AES analysis in combination with sputter etching in argon, small changes in the argon concentrations in the films may not have been detected. In addition, only very small quantities of argon are normally observed in crystalline films deposited without substrate bias applied [36, 37]. If argon incorporation was responsible for the lattice expansion, similar expansions should also have been observed in the TiC and TiC$_x$N$_y$ cases. A model which has been successfully used to explain intrinsic tensile stresses generated during thin film growth is the grain boundary relaxation model [40, 41] proposed by Doljack and Hoffmann. According to this model, the stress is generated in the grain boundaries and it is inversely proportional to the grain size. Since dislocation mobility and generation are low at low temperatures in carbides and nitrides [18], a stress generated at the grain boundaries may generate an expansion of the lattice. However, if the coating does not consist of grains with dense intercrystalline boundaries, the stresses generated can be relaxed.
Fig. 10 Lattice parameter for TiC$_x$N$_y$ films as a function of composition. The shaded area represents bulk results [32-34].
at open voided boundaries between grains and columns. Since, as measured from X-ray line broadening, the TiN phase has a grain size of about 35 nm and a fully dense structure only around stoichiometric composition an expansion may be generated in this region. This is also the region where a deviation from the bulk lattice parameter is observed. According to the grain boundary relaxation model, the strain, $\epsilon$, is given by:

$$\epsilon = \frac{1}{1-\nu} \frac{\Delta}{D}$$  \hspace{1cm} (1)

where $\nu$ is Poisson's ratio, $\Delta$ the grain boundary relaxation distance and $D$ the grain size. If a grain size of 35 nm is used together with a value of the grain boundary relaxation distance of 1Å [36] and a Poisson's ratio of 0.2 [17], a tensile strain of 0.36% is calculated. The observed maximum expansion of the lattice parameter is 0.33% in a very good agreement with this value. The fact that no expansion of the TiC lattice was noticed even though a small grain size was measured can accordingly be explained by the open structure of the films (see Figs. 2 and 3). The proposed mechanisms can also explain results reported by other workers. Igasaki and Mitsuhashi [9] have, e.g., shown that the lattice parameter of TiN increases from 4.24 to 4.25 and that the grain size decreases from 50 nm to 20 nm when a substrate bias of -100 V is applied. They also measured the resistivity of the films and it was found to decrease from 200 $\mu\Omega$-cm to 24 $\mu\Omega$-cm for films deposited with bias. The decrease in resistivity is probably due to a higher density of the films (see section 3.4) and the increase in lattice parameter can thus be explained.

The grain size for the TiN phase is as already mentioned about 35 nm for films near or above stoichiometry. For films with a lower nitrogen content the grains are larger, at $\frac{N}{TT} = 0.88$ a size of 65 nm is measured.
When the $\epsilon$-$\text{Ti}_2\text{N}$ phase starts to appear the grain size of the $\delta$-TiN phase immediately drops and becomes about 25-35 nm. The grain size is also affected by the power applied to the target during the deposition. In Fig. 11 the grain size is plotted versus the applied power. Results for two different nitrogen partial pressures are shown.

3.3 Microhardness

Microhardness values versus nitrogen and carbon content in the deposited films are shown in Fig. 12. For the Ti-C case the hardness increases with increasing C/Ti ratio and approaches for $\frac{C}{Ti} = 1$ a value of 2800 kpm$^{-2}$ which is close to the bulk value. For higher carbon concentrations the hardness increases rapidly and approaches 4000 to 5000 kpm$^{-2}$. As we have shown earlier [1] carbon is deposited both on the substrate and target surfaces when the methane content in the sputtering gas becomes high enough. The produced films are similar to diamond like or i-carbon films that are also known to be very hard [42, 43]. Below C/Ti = 1 a decrease in hardness is also expected since a lower carbon content decreases the number of electrons in the bonding portion of the d-band and hence lowers the bond strength [18]. The decrease is, however, not as rapid as that observed in bulk TiC samples. Using nitrogen as the reactive gas, the hardness of the films also increases rapidly as nitrogen is added to the structure. Above N/Ti = 0.3, the increase is less rapid, but continues until a value of about 2200 kpm$^{-2}$ is reached at stoichiometry. Above N/Ti = 1.0, a rapid decrease in hardness is observed. These results agree well with published results [11, 17] at both low and high nitrogen concentrations. In the region $0.2 \leq N/Ti \leq 0.9$ higher hardness values have been reported with a maximum of 3500 kpm$^{-2}$ at a N/Ti ratio of about 0.6 [10, 17]. The differences may be due to the open structures observed in our
Fig. 11 Grain size of $\delta$-TiN films versus applied power. Results are shown for two different partial pressures of the reactive gas.
Fig. 12  Vickers hardness for Ti-C and Ti-N films as a function of composition. Bulk values taken from Ref. [18] are also shown.
films in this composition range. Such a reason has also been proposed earlier [16] to account for the very low hardness values obtained at hyperstoichiometric composition reported in the literature [10, 16, 17].

3.4 Electrical resistivity

The variation of electrical resistivity with composition is shown in Fig. 13 for both the Ti-N and Ti-C systems. It is seen that for the Ti-N system, a maximum value of about 200 $\mu\Omega$-cm is reached at $\frac{N}{Ti} = 0.25$. Above this ratio the resistivity decreases and reaches a minimum of 25 $\mu\Omega$-cm at $\frac{N}{Ti} = 0.98$. For hyperstoichiometric films, the resistivity increases again. At the maximum resistivity the temperature coefficient of resistivity (TCR) reaches a minimum of about 100 ppmK$^{-1}$. For stoichiometric TiN, the TCR is found to be 950 ppmK$^{-1}$. For the Ti-C system the resistivity increases from about 70 $\mu\Omega$-cm for pure Ti to about 250 $\mu\Omega$ cm for stoichiometric TiC. For higher C/Ti ratios, carbon is deposited as mentioned earlier, direct from the plasma and for films with $\frac{C}{Ti} \approx 3-5$ the resistivity is 2800 $\mu\Omega$-cm. The value of the TCR decreases from 1700 ppmK$^{-1}$ for pure Ti samples to -50 ppmK$^{-1}$ for TiC$_{1.0}$. The resistivity of titanium carbonitride films is shown in Fig. 14. A maximum resistivity of about 600 $\mu\Omega$-cm is reached for films with the composition TiC$_{0.67}$N$_{0.33}$. The changes in electrical resistivity for carbides and nitrides can usually be attributed to one or more of the following factors [18] (i) different composition (ii) impurities especially interstitially-incorporated elements such as oxygen and (iii) residual porosity. For thin films defects incorporated during growth and perhaps more important the small grain size obtained also affect the resistivity. Bulk values of resistivity are for TiN about 25 $\mu\Omega$-cm and for TiC about 60 $\mu\Omega$-cm [18]. The resistivity for stoichiometric TiN film agrees accordingly very well with reported bulk data, but for stoichiometric TiC samples, a
Fig. 13  Electrical resistivities as functions of composition for Ti-C (o) and Ti-N (●) films.

Fig. 14  Electrical resistivity versus composition for TiCN films.
large discrepancy is observed. However, as mentioned above, the density of the samples may influence the resistivity to a large extent, and was shown in section 3.1 while stoichiometric TiN has a density which corresponds to the bulk value, the density of TiC$_1$ is much lower than that of the bulk. Corrections for such deviations from bulk densities can be made using an empirical formula of the type [18]:

$$\rho_A = \rho_M \cdot P^{3.5}$$  \hspace{1cm} (2)

where $\rho_M$ is the on the sample measured resistivity, $\rho_A$ the actual resistivity for a sample with full density and $P$ the ratio of the sample and X-ray densities. For TiC$_1$ $P$ is found to be equal to 0.71 and thus an actual resistivity of 80 $\mu\Omega$-cm is calculated from (2). This value lies within the scatter of reported bulk resistivities. If the variation in the resistivity in Fig. 13 is compared with the behaviour of the film density for the Ti-N system (see Fig. 3) it is seen that for compositions where maxima occur in the former a minima are observed in the latter and "vice versa". Thus, one of the major reasons to the deviation of the resistivity of carbide and nitride films from bulk values seems to be the porosity in the form of an open structure with voided grain boundaries (see Fig. 1 and 2).

The measured TCR also supports this interpretation. The TCR can be shown to be reduced due to both surface scattering and impurity effects [44] and hence films with an open type 1 zone structure will have very low values of TCR. For the films studied, the lowest values were found at $\frac{N}{TT} = 0.25$ and $\frac{C}{TT} = 1.0$.

The influence of grain size on resistivity seems to be small, since even if the grain size in stoichiometric TiN is of the same order as the mean free path of the electrons in the material [44] a resistivity value close to the bulk value is found.
4. DISCUSSION

As discussed in section 3 TiN films prepared by reactive sputtering show a dense structure only in a narrow composition range around the stoichiometric composition, and prepared Ti-C films do not have such dense structures as bulk TiC. Also, even if they are small (35 nm) the grain sizes of the TiN$_{1.0}$ films are almost a factor of two larger than those of the TiC$_{1.0}$ films. It has earlier been shown [1] that the composition of the films was to a large extent governed by the reactions occurring on the target surface. The main part of the flux of atoms from the target impinging on the substrates consists of Ti and C or N atoms (or ions), even if molecules (TiC or TiN) can also be present to a minor extent [2, 3]. The structures and morphologies of the resulting films will to a large extent depend on the mobility of the impinging atoms on the surface before they condense and become entrapped in the film. One of the most important parameters determining the mobility of the adatoms is the substrate temperature. However, it has recently been shown [29, 45] that chemical potentials can also influence adatom mobility to a large extent. In that work the formation of outgrowths during co-evaporation of Ni-Al films with 30-45 at.% Al was explained as a directed atomic migration under the influence of a chemical potential. The potential was expressed in terms of the free energy of formation of the $\beta'$-NiAl phase which is the most stable phase in the Ni-Al system. The free energy of formation, which to a good approximation can be set equal to the heat of formation $\Delta H$, can also affect the growth of compounds such as carbides and nitrides. Since the heat of formation is negative and has its highest numerical value at around stoichiometric composition [18], there will be a strive to form regions in the film with this composition. When the amount of non-metal atoms or ions on the surface are smaller than the amount of metal atoms, composition gra-
dients and thus chemical potentials may develop. A directed migration of the pre-condensed species may thus occur leading to the formation of relatively large stoichiometric grains surrounded by substoichiometric regions and voided boundaries [29, 45]. However, if the substrate temperature becomes high enough to allow thermally-activated surface diffusion ($T/T_m > 0.3$) to be dominating the effect of chemical potentials will not be as pronounced [29, 45]. As the amount of nitrogen or carbon on the surfaces increases, the composition gradients and the directed migration will decrease. This implies that smaller grains with denser grain boundaries will form as the composition approaches stoichiometry. For TiN films, such a variation in grain size and morphology is also observed. For TiC films the grain size also decreases as the composition approaches stoichiometry, but no films with full density have been observed. However, as described by Ritchie [25], this may be due to free carbon located in the grain boundaries.

When a stoichiometric compound is formed, the grain size is governed by thermal diffusion of the adatoms, at least for $T/T_m > 0.3$, but for stable compounds with free energies of formation which are negative, energy is also liberated at the formation of the compound and this can also affect the adatom mobility. For TiN and TiC there is a difference of almost a factor-of-two between the heats of formations. The difference in grain size between these compounds is also about a factor-of-two. To make a further test of this relation between the heat of formation and grain size we have also made some preliminary studies on reactively sputtered tungsten carbide. These coatings which were prepared under the same conditions as the TiN and TiC samples ($T = 775$ K and $P_{CH_4} = 1 \times 10^{-3}$ torr) consist of $\beta$-WC with a grain size of 5 nm. ($\beta$-WC is a high temperature phase with B1 structure and $a_0 = 4.22$ Å). The grain sizes of TiN, TiC and $\beta$-WC versus
the heat of formation of the compounds\cite{18} are plotted in Fig. 15.
Since only the heat of formation for \( \alpha \)-WC is available this value is used, but there of course is an uncertainty in the value of \( \Delta H \) for \( \beta \)-WC. For the carbides the influence of free carbon in the grain boundaries may, as mentioned above, lower the grain sizes. However, even if this is the case, it can be stated that, since the three materials studied have the same crystal structure and are deposited at almost the same homologous temperature \( 0.23 < T/T_m < 0.25 \), a higher (negative) heat of formation implies a larger grain size.

In section 3.2.2, it was shown that the grain size increases as the power applied to the target increases. An increase in power results in both a larger flux of atoms impinging on the substrate and an increase of the energy of each atom. If the impinging flux is small, the migrating adatoms will have a low probability of collision and the increase in energy of the incoming particles with power results in larger mean migration paths and thus larger grain sizes. When the impinging flux becomes high enough, the collision probability will increase thereby reducing the grain size \cite{46, 47}. Such high fluxes have not been studied in this work. However, during reactive sputtering another effect that occurs when the power increases can also increase the grain size of the deposited films. Increase in power results in a reduction of the fraction of molecules sputtered from the target \cite{48}. Since molecules have lower mobilities than single atoms \cite{49}, a reduction in the number of migrating TiN or TiC molecules results in increased grain size.

In section 3, it was also shown that an open structure (zone 1) develops when a two-phase structure is present. The grains are small and large strains are present. For the Ti-N system this is also expected, since one of the two nitride phases, the \( \epsilon \)-Ti\(_2\)N phase, has a tetragonal
Fig. 15 Grain size as a function of the heat of formation of the compound. The heat of formations are taken from Ref. [18]. Since the value for β-WC is not available, the value for α-WC has been used and hence the value shown must be treated with caution.
structure and thus a low symmetry which makes it difficult to develop, non-stressed dense structures. To produce dense films consisting of either $\alpha$-Ti or $\epsilon$-Ti$_2$N or $\epsilon$-Ti$_2$N$_x$-TiN or even single phase $\epsilon$-Ti$_2$N, an additional amount of energy must be supplied to the migrating adatoms. This can be done either by raising the substrate temperature to above 775 K or by applying a substrate bias. For the Ti-C system a distortion of the structure was also noticed in the two phase region. In this region the lattice in the TiC grains is expanded.

5. CONCLUSION

In this work it has been shown that the free energy of formation of a compound plays an important role in the formation process of reactively sputtered carbide and nitride films. A high value of the free energy of formation leads to high adatom mobility and thus larger grain size. It has also been shown that the morphology of the films obtained to a large extent determines the electrical and mechanical properties of the coatings. The large lattice parameter that normally is observed for TiN coatings is explained using the grain boundary relaxation model developed by Doljack and Hoffman [40, 41].

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MECHANISMS OF REACTIVE SPUTTERING OF TITANIUM NITRIDE
AND TITANIUM CARBIDE

III INFLUENCE OF SUBSTRATE BIAS ON COMPOSITION AND STRUCTURE

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Films of TiN and TiC have been grown by reactive r.f. sputtering of titanium in mixed Ar-N₂ and Ar-CH₄ discharges on negatively-biased substrates. The compositions of the films were measured using Auger electron spectroscopy and their structure and morphology studied using X-ray diffraction and scanning electron microscopy respectively. The composition was found to be strongly affected by the bias voltage. An increase in bias increases both the carbon and nitrogen contents in substoichiometric films. However, when stoichiometric $\delta$-TiN is formed, no further change in the composition occurs. For TiC films an increase above C/Ti = 1.0 is possible. The structure is also affected by the bias voltage. For example the grain size of TiN has a maximum at a bias of -200 V. A possible explanation is a double influence of the ion bombardment. At low voltages, the adatom mobility is enhanced and the grain size increases but as the bias increases resputtering of species from the growing film surface becomes increasingly important and the grain size decreases.
1. INTRODUCTION

In parts I and II of this work [1, 2], we have shown how the composition, structure and morphology of titanium reactively r.f. sputtered in nitrogen and methane on to non-biased substrates held at 775 K were affected by process parameters. Among other things it was shown that dense TiN films were only obtained in a narrow range around stoichiometric composition and that the TiC films obtained had an open structure with low density. In order to overcome these problems and to be able to produce dense TiN and TiC films over a wider range of partial pressure additional energy has to be brought to the growing film. This can be done either by raising the substrate temperature or by bombarding the films with ions during the growth. To give the adatoms on the growing film a sufficiently large thermal mobility the substrate temperature, $T$, must exceed $0.3 T_m$ where $T_m$ is the melting temperature of the deposited material. This implies that the substrate temperature must exceed 970 K for TiN and 1000 K for TiC [4]. However, these substrate temperatures are far too high for many applications e.g., if depositions on high-speed steels are to be performed, the substrate temperature should not exceed the annealing temperature of the steel, which is typically about 830 K. Instead, ion bombardment of the growing films can be used to change their structure and morphology. Low energy ion bombardment of thin films during growth has been studied by a large number of workers [5-13]. Changes in nucleation characteristics [5, 6] as well as changes in morphology [7, 8], composition [9, 10], crystallinity [11, 12] and defect concentration [13] of the films have been reported. A feature underlying many of the ion-bombardment induced effects mentioned is enhanced diffusion. For example it has been clearly demonstrated by Marinov [5] that ion bombardment enhances adatom mobility during the deposition of silver. Both the nucleation characteristics and
the film structure were shown to be affected. Another effect occurring which has also been shown to be very important is that of the resputtering of condensed and migrating species [7-9, 14]. So far as the reactive sputtering of TiC or TiN films is concerned only a few papers treating influence of substrate bias during deposition have been presented [15, 16]. The objective of this work is to determine the effect of bias on the structural and compositional characteristics of r.f. sputtered TiC and TiN films.

2. EXPERIMENTAL

The depositions were performed in an r.f. diode sputtering system in mixed Ar-N₂ and Ar-CH₄ discharges. A detailed description of the experimental equipment has been given elsewhere [1]. The depositions were carried out at two different partial pressures of each reactive gas. These pressures were 5x10⁻⁵ torr and 5x10⁻⁴ torr for nitrogen and 2.5x10⁻⁴ and 5x10⁻⁴ torr for methane. These partial pressures were chosen since on non-biased substrates stoichiometric compounds are obtained at the higher pressure and films with N/Ti and C/Ti ratios of about 0.5 at the lower pressures (see Ref. [1]). The total pressure was in all cases kept constant at 5x10⁻³ torr. The net r.f. power was also kept constant at 1000 W which is equivalent to a target d.c. offset voltage of 3.6 kV and a current density of 1.6 mA cm⁻². The substrates of polished steel, copper foils and alumina were kept at a temperature of 775 K and at bias voltages ranging from 0 to -700 V. Films were deposited to thicknesses ranging from 0.3 to 2 μm. The composition of the films obtained was determined using Auger electron spectroscopy (AES). A detailed description of the quantitative procedure is given in Ref. [17]. Using this method an accuracy of about 5 percent is obtained in the composition ranges investigated in this work.
The microstructure and crystallographic structure were identified using X-ray diffraction analysis. The diffraction pattern was recorded with a Guinier camera using filtered CuKα₂ radiation. The grain sizes were estimated from the width of the X-ray diffraction lines using Scherrer's formula [18]. Instrumental broadening was corrected for using reference lines from KCl powder [18]. For the TiC films broad and poorly-defined peaks were observed and the error limits of both the grain size and the lattice parameter are thus large. For TiN films the peaks were much better defined and thus smaller error limits are obtained. The morphologies of the films were studied using a scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1 Composition

The variations in composition with substrate bias of reactively sputtered titanium in methane and nitrogen are shown in Figs. 1 and 2 respectively. Results are shown for the two partial pressures used in each case. For titanium sputtered at a methane partial pressure of 5x10⁻⁴ torr the carbon-to-titanium ratio is found to increase with negative bias and reach a maximum value of 1.08 at -200 V. When the bias is increased further the ratio decreases and approaches 1.00. For films sputtered at a lower partial pressure (P_{CH₄} = 2.5x10⁻⁴ torr) an increase from C/Ti = 0.56 to 0.88 is observed when the bias increases from 0 to -500 V. For films sputtered in nitrogen no change in film composition with bias is observed for films sputtered at P_{N₂} = 5x10⁻⁴ torr. For films sputtered at the lower pressure (P_{N₂} = 5x10⁻⁵ torr) the nitrogen-to-titanium ratio increases from 0.35 to 0.70 as the bias increases from 0 to -700 V.
Fig. 1  Carbon concentrations in deposited films vs. substrate bias voltage. Results are shown for two different methane partial pressures (given in torr).

Fig. 2  Nitrogen concentrations in deposited films vs. substrate bias voltage. Results are shown for two different nitrogen partial pressures (given in torr).
When a negative substrate bias is applied to the substrates the number of ionized molecules and atoms in the plasma increases. The energetic electrons from the target strike the substrate and cause emission of secondary electrons which are accelerated into the plasma by the bias field. Since the ionization probability due to electron impact has a maximum at about 100-150 eV for most gases [19], the electrons accelerated by the bias field are effective in increasing the ionization of the plasma. The total number of ions of argon, methane or nitrogen impinging on both the target and substrate surfaces increases. As the bias increases the energy of the species impinging on the substrate also increases as does the resputtering. These effects are usually observed in the behaviour of the deposition rate which has a maximum for a bias voltage of around -100 V [10, 20]. This is also the case in these experiments, an increase of about 20 percent being noted at -100 V for TiN.

We have earlier shown that when a mixed Ar-N\textsubscript{2} ion beam impinges on a titanium surface a nitriding of the surface layer occurs [21]. If the ratio between the argon and nitrogen fluxes is kept constant the amount of nitrogen entrapped at the surface increases with the total impinging flux and energy until δ-TiN is formed on the surface. The flux was found to have a higher effect than the energy. The increased amount of nitrogen and carbon in the films with increased bias voltage at low pressures and the absence of any composition change when stoichiometric δ-TiN is formed are thus in agreement with what was observed in the ion beam bombardment experiments. For the Ti-C case as already mentioned C/Ti increases above 1.00 and reaches a maximum of 1.08 at -200 V. The increase above unity is understandable since it is known that a direct deposition of carbon can occur during sputtering in hydrocarbons [1, 16, 22]. The decrease above -200 V can be explained in terms of resputtering. Since the sputtering
yield increases with energy more material is resputtered when the bias increases. Depending on the bond strength between the different species on the growing film surface preferential sputtering may occur. For Ti-N samples of different compositions a small effect of preferential sputtering occurs [17]. For samples which do not contain the single δ-TiN phase Ti is preferentially sputtered whereas in samples with δ-TiN a small tendency to a depletion of nitrogen was observed. For Ti-C samples, no preferential sputtering was found [17]. This is in agreement with results obtained by Wehner [23] on stoichiometric TiC samples. In the case of a growing film, however, the situation may be quite different, since the bond strength is lower for migrating adatoms. For example on a growing film with excess carbon an increase in bias may result in a preferential resputtering of carbon adatoms. Since fewer stable condensation (nucleation) sites are available for excess carbon adatoms than for titanium adatoms, the probability of resputtering will be higher. This explains the observed decrease in the C/Ti ratio above -200 V for films sputtered at a methane partial pressure of 5x10^-4 torr. For films deposited at lower partial pressures where substoichiometric TiC or both Ti and TiC are formed, the effect of resputtering will not be a decrease in the carbon content but rather an increase. The same is true for substoichiometric TiN films.

3.2 Crystallographic structure

The lattice parameter versus substrate bias for films sputtered at partial pressures of methane and nitrogen of 5x10^-4 torr is shown in Fig. 3. Whereas a continuous decrease with increasing substrate bias is observed for TiN, the lattice parameter for TiC increases from the bulk value at zero bias to a maximum at -300 V. Beyond this bias the lattice parameter decreases and approaches the bulk value for TiC at higher substrate bias.
Fig. 3 Lattice parameters for films sputtered at $P_{CH_4} = 5 \times 10^{-4}$ torr (o) and $P_{N_2} = 5 \times 10^{-4}$ torr (•) vs. substrate bias voltage. Also shown in the figure are the bulk values for stoichiometric TiC and TiN.
voltages. For TiC sputtered at the lower methane partial pressure the lattice parameter increases continuously from 4.302 to 4.325 as the bias increases. TiN films deposited at \(5 \times 10^{-5}\) torr exhibit a two-phase structure of \(\varepsilon\)-TiN and \(\delta\)-Ti\(_2\)N except at the highest bias voltage, where a \(\delta\)-TiN structure is observed.

If a negative bias is applied to the substrates during sputtering it has been reported [7, 24, 25] that compressive stresses occur in the films. The reasons for this are not fully known but an increased entrapment of argon with increasing bias has been suggested [7, 25]. Hoffman and Thornton [26, 27] also reported high compressive stresses for films sputtered at low working gas pressures at zero bias. They explain their findings to be due to an "atomic peening" mechanism, working gas atoms reflected at the cathode impinging on the growing film with a momentum of impact sufficient to disturb the condensed material and pack it together.

The incorporation of argon in sputtered films has been studied [28, 29] and it has been shown that amorphous materials can incorporate much larger concentrations of gas atoms than crystalline materials. This has been explained as being due to the fact that amorphous materials have a higher concentration of available incorporation sites large enough to accomodate the gas. Thornton and Hoffman [30] have found that the amount of argon incorporated in metals depends on the mass ratio between the coating material and the working gas. As this ratio approaches one, the concentration of entrapped gas decreases below the detection limit (0.01 at.%) for the electron microprobe method used [30]. This implies that very low concentrations of argon in titanium and titanium-nitride and -carbide films should be expected in our case. Also, no indications of an increasing argon incorporation with bias voltage were noticed during the AES analysis. However, since we used AES analysis in combination with sputter etching in argon, changes in argon concentration may not have been detected.
For TiN, the lattice parameter decreases with increasing ion bombardment. The expansion of the lattice parameter at zero bias voltage has been explained elsewhere [2] using the grain boundary relaxation model proposed by Hoffman [31]. For bias voltages higher than -200 V a compression of the lattice is observed. This may be due to a distortion of the lattice by momentum impact, "atomic peening" as discussed above.

For the Ti-C case an expansion of the lattice with increased bias voltage is observed. In Fig. 4 the lattice parameter for TiC is plotted as a function of composition for our films and for bulk TiC [32]. It is seen that up to C/Ti = 1.0 the lattice parameter for the films follows the variations for bulk TiC. It should, however, be noted that the values of the lattice parameter with bias applied to the substrates are on the lower limit of the region reported for bulk data [32] indicating that the ion bombardment may have caused a compression even in this case. When the C/Ti ratio exceeds 1.0, the lattice parameter shows an almost linear increase with carbon concentration. In this region the equilibrium phase diagram [32] shows a two phase structure of TiC and carbon. However, if the excess carbon present in the films was completely agglomerated as a second separate phase no large shifts in the lattice parameter should have been observed. An explanation is therefore that excess carbon seems to occupy interstitial positions of the TiC lattice thereby causing a distortion of the lattice and hence a shift in the lattice parameter towards higher values.

The change in grain size with substrate bias is shown in Fig. 5 for films sputtered at partial pressures of methane and nitrogen of 5x10^-4 torr. Whereas the grain size in the TiC films decreases monotonically with bias an increase towards a maximum value at -200 V occurs in the TiN films.
Fig. 4  Lattice parameter of TiC as a function of composition. Results obtained at two different methane partial pressures $2.5 \times 10^{-4}$ torr (*) and $5 \times 10^{-4}$ torr (o) are shown together with the bias voltages used. The shaded area represents bulk data from Ref. [32].
Fig. 5  Grain sizes for films sputtered at $P_{\text{CH}_4} = 5 \times 10^{-4}$ torr (o) and $P_{\text{N}_2} = 5 \times 10^{-4}$ torr (•) vs. substrate bias voltage.
Ion bombardment during film growth changes the microstructure and morphology of the obtained coatings. As already mentioned, these changes can be attributed to resputtering effects and to enhanced mobility of adatoms. In the Ti-N case, the increase in grain size at bias voltages below -200 V can be attributed to increased adatom mobility due to a momentum transfer from the bombarding ions. When the bias is increased further, the effects of preferential sputtering will be increasingly pronounced. Since, in general, the bond strength between an adatom and atoms in the condensed film is lower than that between atoms incorporated in the film, an adatom may be preferentially sputtered. An enhanced resputtering will thus be observed as a reduction in adatom mobility. Furthermore, as the energy of the impinging ions increases, penetration into the lattice of the condensed film and the generation of defects increase. This gives rise to an increased number of preferential nucleation sites resulting in smaller grains and a destruction of the columnar growth morphology. The latter can also be observed in the cross-sections of TiN films shown in Fig. 6.

For stoichiometric TiC films, the grain size decreases with substrate bias. However, since a bias increase up to -200 V results in an increase in the C/Ti ratio even above unity, the excess carbon can reduce the adatom mobility and hence the grain size. However, also for substoichiometric films prepared at the lower methane partial pressure, the grain size decreases with increasing bias. We have earlier shown [2] that the grain size decreases for single-phase TiC and $\delta$-TiN film deposited on non-biased substrates, as the composition approaches stoichiometry. If this effect is stronger than the ion-bombardment enhanced diffusion, the net effect of an increasing bias on the grain size of substoichiometric films may actually be a decrease.
Fig. 6  Scanning electron micrographs showing cross-sections of films sputtered at $P_{N_2} = 5 \times 10^{-4}$ torr and at different bias voltages a) 0 V, b) -200 V and c) -700 V.
4. **SUMMARIZING REMARKS**

It is shown in this work that a negative substrate bias affects both the composition and structure of TiN and TiC deposits. For both compounds an increase in substrate bias increases the non-metal content in the films. However, for the Ti-N case no further increase in nitrogen content occurs when stoichiometric $\delta$-TiN is formed. For TiC films an increase above $C/Ti = 1.0$ is possible.

The structural changes that occur when a substrate bias is applied during deposition are mainly effects of resputtering, ion bombardment enhanced diffusion and "atomic peening". However, since composition also changes with substrate bias, this gives rise to structural changes. For stoichiometric $\delta$-TiN, the lattice parameter is found to decrease with increasing ion bombardment in accordance with the atomic peening arguments presented by Thornton and Hoffmann [26, 27]. For TiC films, the lattice parameter is strongly affected by the amount of carbon in the films and for $C/Ti$ ratios above unity the variations in lattice parameter are associated with interstitially-incorporated carbon atoms. The observed changes in grain size are explained in terms of ion-bombardment enhanced diffusion of the adatoms and resputtering. For stoichiometric $\delta$-TiN films, the enhanced adatom mobility causes the grain size to increase for bias voltages below -200 V. At higher bias voltages resputtering of adatoms becomes dominating and the grain size decreases. For TiC the compositional changes that occur with bias cause the grain size to decrease even for low bias voltages.

The results obtained in this work imply that in order to produce high-quality TiN films a relatively low bias voltage should be applied and on the basis of earlier observations [4] a high degree of ionization and thus high current densities should be used. It should, however, be pointed
out that if the flux of ions towards the substrate is too high, the deposition rate decreases. For TiC films, the situation is somewhat different since stresses due to interstitially-incorporated carbon may result if the bias voltage used is too low. In this case as high bias voltage as possible without reducing the deposition rate too much is preferable.

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REFERENCES


