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# Water as reactive gas to prepare titanium oxynitride thin films by reactive sputtering

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## Abstract

Thin films of titanium oxynitride were successfully prepared by dc reactive magnetron sputtering using a titanium metallic target, argon, nitrogen and water vapour as reactive gases. The nitrogen partial pressure was kept constant during every deposition whereas that of the water vapour was systematically changed from 0 to 0.1 Pa. The evolution of the deposition rate with an increasing amount of water vapour injected into the process was correlated with the target poisoning phenomenon estimated from the target potential. Structure and morphology of the films were analysed by X-ray diffraction and scanning electron microscopy. Films were poorly crystallised or amorphous with a typical columnar microstructure. Nitrogen, oxygen and titanium concentrations were determined by Rutherford backscattering spectroscopy and nuclear reaction analysis, and the amount of hydrogen in the films was also quantified. Optical transmittance in the visible region and electrical conductivity measured against temperature were gradually modified from metallic to semiconducting behaviour with an increasing supply of the water vapour partial pressure. Moreover, an interesting maximum of the electrical conductivity was observed in this transition, for a small amount of water vapour.

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**Keywords:** Titanium oxynitride; Reactive sputtering; Water vapour

## 1. Introduction

During the past 5 years, there has been considerable interest in the production of metallic oxynitride thin films, since the presence of oxygen in nitride compounds leads to unexpected and promising functional range of materials. Various chemical and physical deposition techniques have been implemented to prepare oxynitride coatings with a tuneable N/O ratio and consequently, with a wide range of properties [1–4]. Even if silicon oxynitride films have lately deserved great attention due to their technological importance in microelectronics [5–7], few works have been devoted to transition-metal oxynitrides [8–11]. Recent articles have been focused on titanium oxynitride thin films since these materials

reveal behaviours included between metallic TiN and resistive TiO<sub>2</sub> compounds [12,13]. Besides, such oxynitrides usually exhibit a complex structure, the first problem which occurs with the preparation of TiO<sub>x</sub>N<sub>y</sub> films with various metalloid concentrations. Reactive magnetron sputtering is an attractive way to deposit these films. A metallic target sputtered in a mixed reactive working gas (O<sub>2</sub>+N<sub>2</sub>) [14,15] or the reactive gas pulsing technique [16,17] can be used to modify N/O ratio in the films.

In the present work, we report on the use of water vapour as reactive gas to deposit titanium oxynitride coatings by dc reactive magnetron sputtering. The influence of the water vapour partial pressure on some process parameters (deposition rate, target potential) is investigated taking into account the poisoning phenomenon at the surface of the target. A systematic increase of the water vapour partial pressure leads to crystallised

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titanium nitride or completely amorphous oxynitride and oxide compounds with a typical columnar microstructure. Optical characteristics measured in the visible region show that  $\text{TiO}_x\text{N}_y$  films prepared with low water vapour partial pressure are mainly absorbent, whereas a high water supply tends to produce transparent and interferential titanium dioxide coatings. The chemical composition is also determined in relation to the varied water vapour partial pressure. The reverse evolution of oxygen and nitrogen concentrations is correlated with the decrease of the electrical conductivity and the metallic-semiconducting behaviours of the titanium oxynitride thin films.

## 2. Experimental

The depositions of titanium oxynitride thin films were performed in a home-made high vacuum reactor, whose volume was approximately 60 l. Substrates were introduced into this reactor through a 1 l airlock. A metallic titanium target (purity 99.6%, 50 mm diameter) was dc sputtered with a constant current density  $J_{\text{Ti}} = 51 \text{ A m}^{-2}$ , while the substrates (glass and (100) silicon wafers) were grounded and kept at a constant temperature,  $T_s = 293 \text{ K}$ , during the deposition. It was located at a distance of 50 mm from the substrate. Substrates were ultrasonically cleaned with acetone and alcohol and also before each run, Ti target was pre-sputtered in a pure argon atmosphere for 5 min in order to clean the surface of the target. The deposition rate of pure Ti is  $510 \text{ nm h}^{-1}$  with target potential  $U_{\text{Ti}} = 275 \text{ V}$  and argon pressure  $P_{\text{Ar}} = 0.4 \text{ Pa}$ . Argon and nitrogen partial pressures were maintained at 0.4 Pa and 0.1 Pa, respectively, using mass flow controllers and a constant pumping speed  $S = 10 \text{ l s}^{-1}$ . Such operating conditions correspond to the nitrated sputtering mode of the process (target potential  $U_{\text{Ti}} = 314 \text{ V}$ ). Nitrogen partial pressure is large enough to form TiN compound. The water vapour partial pressure was systematically changed from 0 to 0.1 Pa using a leak valve connected to a de-ionised water flask. In the first approximation, water vapour partial pressure is derived by subtracting nitrogen and argon partial pressure from total pressure (plasma on). The deposition time was adjusted in order to obtain film of equal thickness (close to 400 nm).

The crystallographic structure was investigated by X-ray diffraction (XRD) using monochromatised Cu  $K_\alpha$  radiation in the  $\theta/2\theta$  configuration. Optical properties were analysed from optical transmittance spectra of the film/glass substrate system recorded from a Lambda 20 UV-visible Perkin-Elmer spectrophotometer. Combining Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA), it is possible to perform the elemental analysis of all elements present in the coatings. In order to analyse the heavy element (Ti) in the coatings, a 2 MeV  $\alpha$  particles beam used for the

backscattering experiment was produced by the 2 MV Tandatron accelerator installed at LARN in Namur and the scattered particles were detected in a PIPS (passivated implanted planar silicon) detector placed at  $165^\circ$  relative to the incident beam. The analysis of light elements in the coatings was performed with a 5.2 MeV  $\alpha$  particles beam produced with the same accelerator. The particles due to  $^{14}\text{N}(\alpha, p_0)^{17}\text{O}$  and  $^{14}\text{N}(\alpha, p_1)^{17}\text{O}$  nuclear reactions were detected in a PIPS detector placed at  $90^\circ$  relative to the incident beam. The  $\alpha$  scattered particles were stopped in a 24  $\mu\text{m}$  Mylar foil filter placed in front of the detector. Simultaneously, the scattered  $\alpha$  particles were detected in a PIPS detector at backward angle ( $165^\circ$ ). At this incident energy, the cross sections of the elastic ( $\alpha, \alpha$ ) reaction on light elements is non-Rutherford. Data from the literature were used to take into account for the true cross sections [18–20] in order to obtain realistic simulation of the experimental spectra. Cross sectional scanning electron microscopy (SEM) observations were performed on a JEOL JMS-6400F field emission SEM at an acceleration voltage of 5 kV. The electrical conductivity of the films deposited on glass substrates was measured against temperature using the four probes method.

## 3. Results and discussion

### 3.1. Process characteristics

A typical feature of the reactive sputtering process is the abrupt change of some experimental parameters (especially a sudden drop of the deposition rate) for a given supply of the reactive gas [21]. With water vapour as reactive gas, the deposition rate of titanium oxynitride films is also influenced by the amount of water vapour injected into the chamber (Fig. 1). In spite of a low pumping speed ( $S = 10 \text{ l s}^{-1}$ ) used during the deposition, the rate exhibits a continuous evolution from 151 to 48  $\text{nm h}^{-1}$ , when the water vapour pressure increases from 0 to 14 Pa. For low water supplies ( $P_{\text{H}_2\text{O}} < 10^{-2} \text{ Pa}$ ), deposition rate is slightly reduced to  $130 \text{ nm h}^{-1}$  whereas a maximum is reached for  $P_{\text{H}_2\text{O}}$  close to  $5.0 \times 10^{-2} \text{ Pa}$ . Similar results have been obtained by Martin et al. [16] for the deposition of titanium oxynitride thin films by the reactive gas pulsing technique. In our case, the evolution of the deposition rate vs. water vapour pressure can be explained taking into account the occurrence of a competition phenomenon between the removal by sputtering of a nitride layer at the surface of the target and its substitution by an oxide one.

Actually, the poisoning effect of the target can be assessed from measurements of the Ti target potential (Fig. 2). Without water and up to  $P_{\text{H}_2\text{O}} = 1.2 \times 10^{-2} \text{ Pa}$ , the potential is nearly constant ( $U_{\text{Ti}} = 315 \text{ V}$ ) and corresponds to the nitrated sputtering mode (without nitrogen,  $U_{\text{Ti}} = 275 \text{ V}$  for the metallic sputtering mode).

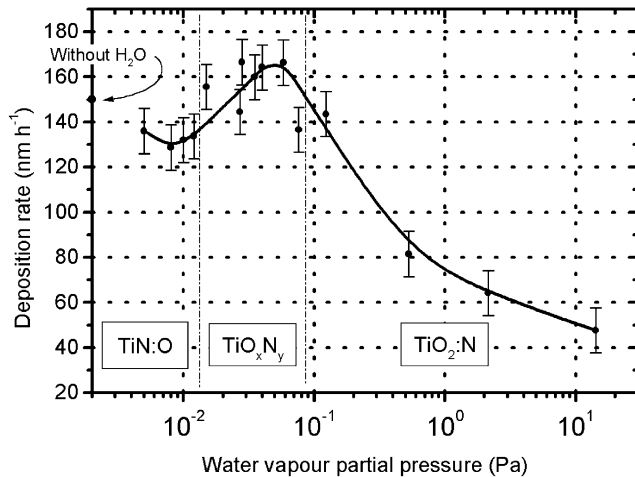


Fig. 1. Deposition rate of titanium oxynitride thin films vs. water vapour partial pressure. A continuous evolution is observed with an increase of the water vapour injection. The change of the deposition rate can be correlated with the occurrence of titanium nitride, oxynitride and dioxide compounds.

For this range of water vapour pressures, as-deposited coatings are titanium nitride compounds with a significant amount of oxygen (orange to brownish colours) namely TiN:O. For water vapour pressures higher than  $P_{\text{H}_2\text{O}} = 7.6 \times 10^{-2}$  Pa, the target potential is near 400 V, which correlates with an oxidised state of the surface of the target. Water injection is high enough to fully run the process in the oxidised sputtering mode. Since the sputtering yield of titanium oxide is lower than that of titanium nitride, the deposition rate largely decreases despite a higher potential. Titanium dioxide thin films are formed with nitrogen as doping (TiO<sub>2</sub>:N).

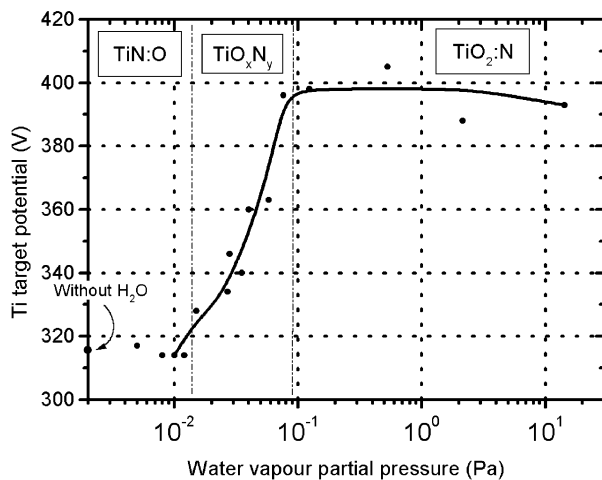


Fig. 2. Titanium target potential  $U_{\text{Ti}}$  as a function of the water vapour partial pressure. Transition from nitrided to oxidised sputtering mode corresponds to an increase of the target potential from 315 to 400 V. This change is gradual and yields to the formation of titanium oxynitride coatings.

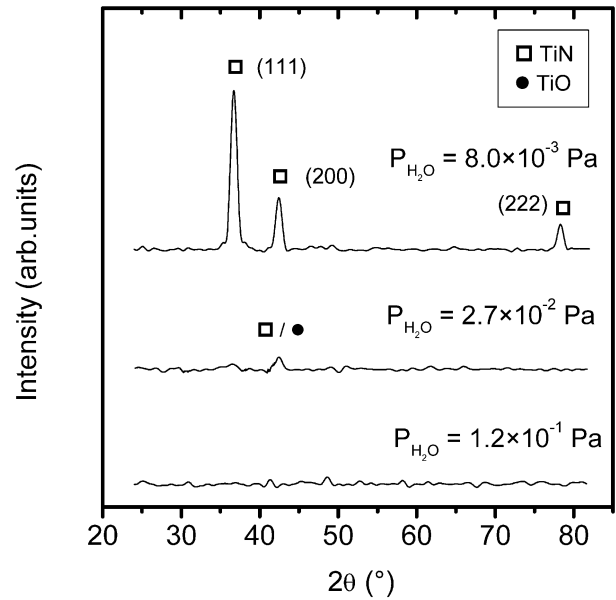


Fig. 3. X-ray diffraction patterns of titanium oxynitride thin films deposited at 293 K on (100) silicon wafers. Films prepared for water vapour partial pressures lower than  $P_{\text{H}_2\text{O}} = 8.0 \times 10^{-3}$  Pa adopt the f.c.c. TiN structure and completely amorphous or poorly crystallised titanium oxynitrides and oxides are obtained for higher pressures.

For  $1.2 \times 10^{-2} < P_{\text{H}_2\text{O}} < 7.6 \times 10^{-2}$  Pa, such water vapour pressures correspond to the highest deposition rates and similarly to a notable increase of the potential from  $U_{\text{Ti}} = 315$  to 398 V. The maximum deposition rate obtained for water vapour pressure close to  $5.0 \times 10^{-2}$  Pa is also due to the competition between a nitrided and an oxidised sputtering mode. The nitrided mode is predominant when water vapour pressure does not exceed  $P_{\text{H}_2\text{O}} = 7.6 \times 10^{-2}$  Pa. Before this pressure value, the energy of ions impinging on the target and so the amount of sputtered particles was increased. Afterwards, the target potential is not so influenced by the water pressure because of the complete formation of an oxide layer on the target with a low sputtering yield (oxidised sputtering mode).

As a result, no abrupt transition from nitrided to oxidised sputtering mode is observed with water vapour as reactive gas (even with a low pumping speed). Instabilities of the reactive sputtering process involving one metallic target and  $\text{O}_2 + \text{N}_2$  as reactive gases [22–25] are avoided, when  $\text{N}_2$  and  $\text{H}_2\text{O}$  are used. Therefore, synthesis of titanium oxynitride compounds with various metalloid concentrations should be favoured using water vapour pressures included between  $1.2 \times 10^{-2}$  and  $7.6 \times 10^{-2}$  Pa.

### 3.2. Structure and chemical composition

X-rays diffraction patterns of the films deposited at room temperature on (100) Si substrates show that the

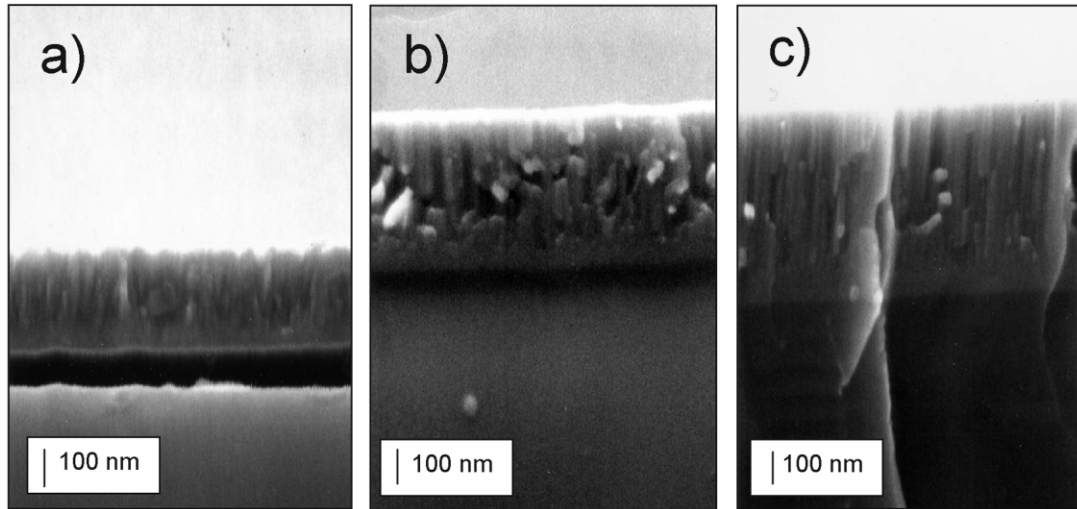


Fig. 4. Cross section observations by SEM of titanium nitride, oxynitride and dioxide thin films prepared with different water vapour partial pressures: (a)  $P_{\text{H}_2\text{O}}=0$  Pa; (b)  $P_{\text{H}_2\text{O}}=4.0\times 10^{-2}$  Pa; (c)  $P_{\text{H}_2\text{O}}=1.2\times 10^{-1}$  Pa. A columnar microstructure is systematically observed.

crystallographic structure is particularly influenced for low water vapour pressures (Fig. 3). Without water and up to  $P_{\text{H}_2\text{O}}=8.0\times 10^{-3}$  Pa, XRD patterns exhibit peaks corresponding to the f.c.c. TiN phase. The crystallite size estimated by the Scherrer's method is approximately 20 nm and a preferential orientation along the (111) direction is systematically observed. This kind of nanostructured compound commonly obtained by others [26–29] vanishes when water vapour pressure exceeds  $8.0\times 10^{-3}$  Pa. The orange-brownish colours of TiN:O coatings change to a metallic or dark green aspect and a nearly amorphous structure is adopted ( $\text{TiO}_x\text{N}_y$ ). Films prepared with water vapour pressures higher than  $1.2\times 10^{-1}$  Pa (transparent  $\text{TiO}_2\text{:N}$ ) also exhibit an amorphous structure. At first, the loss of a long range order with an increase of the water vapour pressure is due to a low surface diffusion of the particles impinging on the substrate or the growing film, since deposits were carried out at room temperature [30,32]. A growth competition between titanium nitride and titanium oxide phases occurs at the surface of growing films in spite of a low water vapour pressure (strong affinity of oxygen with regards to titanium compared to nitrogen). These results are consistent with those found by Bittar et al. [12] and later by Ianno et al. [15] about aluminium oxynitride coatings. They claimed that an addition of small amounts of oxygen in the feed gas during deposition prevents the formation of a crystalline structure. As a result, one can suggest that synthesis of transition metal oxynitride thin films exhibiting a well-crystallised structure requires a substrate temperature of several hundreds Kelvin.

Cross sections of the films observed by SEM systematically show a typical columnar microstructure (Fig. 4a–c). For coatings prepared without water (TiN:O) or

with high water vapour pressures ( $P_{\text{H}_2\text{O}}>7.6\times 10^{-2}$  Pa), such microstructure is expected taking into account Thornton's structure zone model [32]. From melting points of TiN and  $\text{TiO}_2$  ( $mp_{\text{TiN}}=3223$  K and  $mp_{\text{TiO}_2}=2113$  K, respectively) and since deposits were performed at room temperature, the temperature ratio ( $T_{\text{substrate}}/T_{mp}$ ) is lower than 0.13. It corresponds to the zone 1 of the Thornton's model. The processes of surface diffusion are not able to develop in this zone due to little adatom surface mobility. Then, films are formed by narrow columnar grains with a densely packed fibrous morphology. For titanium oxynitride films, the similar microstructure observed in Fig. 4b is not so easy to predict than that of TiN:O or  $\text{TiO}_2\text{:N}$  since few works have been published concerning the physico-chemical properties of such compounds.

SEM micrographs also show that adhesion of the films to the silicon substrate significantly depends on the water vapour pressure. It is worth to mention that fracture cross section of TiN:O films (Fig. 4a) produced a clear detachment of the coating. Adhesion to the surface of the Si substrate seems to have improved for titanium oxynitride (Fig. 4b) and is even better for  $\text{TiO}_2\text{:N}$  films (Fig. 4c) since the fracture of silicon wafer is extended into the coating. At first, due to deposition carried out at room temperature, interdiffusion phenomena at the coating-substrate interface are worsened leading to a poor adhesion (e.g. TiN:O on silicon). In addition, due to the native oxide layer formed on silicon wafers and assuming that a significant amount of oxygen is systematically incorporated into the TiN coatings [33], good adhesion of TiN cannot be reached without sputter cleaning, heating of the substrate and/or biasing during the deposition process. However, interdiffusion and oxygen at the interface are not so detrimental to adhesion

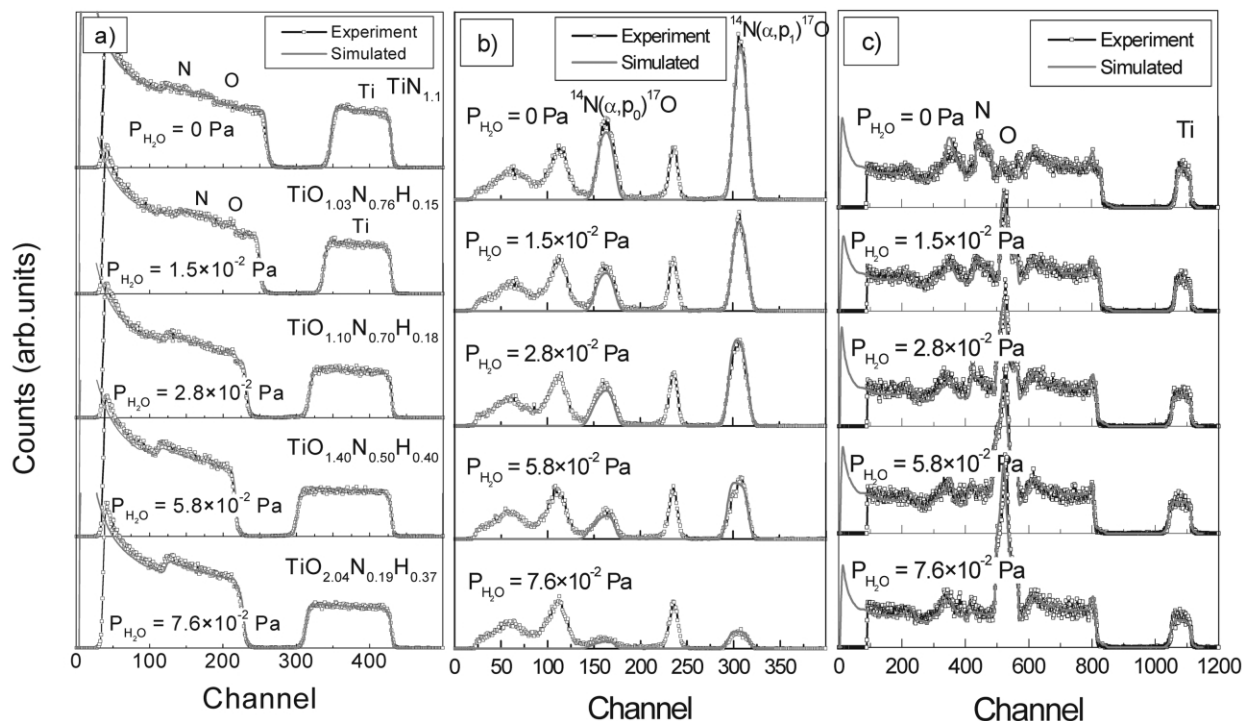


Fig. 5. RBS and NRA spectra of titanium oxynitrides deposited on Si (100) for various water vapour partial pressures. (a) RBS at 2.0 MeV with a backscattering angle of  $165^\circ$ ; (b) NRA at 5.2 MeV with a backscattering angle of  $90^\circ$ ; the two simulated peaks are, respectively, due to  $^{14}\text{N}(\alpha,p_0)^{17}\text{O}$  and  $^{14}\text{N}(\alpha,p_1)^{17}\text{O}$  nuclear reaction and the other peaks are due to reactions on the silicon substrate; (c) RBS at 5.2 MeV with a backscattering angle of  $165^\circ$ .

of titanium oxynitrides and oxides on silicon since no clear detachment of the film to the substrate was observed.

The elemental composition measurements carried out by RBS and NRA show that the water vapour can be used as a reactive gas to modulate the nitrogen and oxygen concentrations. In order to determine oxygen, nitrogen, titanium and hydrogen concentrations, three types of experiments were performed. RBS at 2.0 MeV allowed to determine the amount of titanium knowing the thickness of the films (Fig. 5a) and combined RBS and NRA at 5.2 MeV led to the oxygen and nitrogen concentrations (Fig. 5b,c). The hydrogen composition was finally deduced from simulated RBS spectra at 2.0 MeV. Without water, titanium nitride films are overstoichiometric with a N/Ti ratio of 1.1 (Fig. 6). It is in agreement with numerous studies and models focused on the reactive sputtering of such compounds [31–35]. Nitrogen partial pressure was high enough ( $P_{\text{N}_2}=0.1$  Pa) to maintain the process in the nitrated sputtering mode (cf. Section 3.1) and consequently, TiN films with high nitrogen content were produced.

For low injection of water vapour ( $P_{\text{H}_2\text{O}} < 1.5 \times 10^{-2}$  Pa), oxygen in the film abruptly increases from 6 to 32% because of the very high reactivity of oxygen with regards to titanium (Fig. 6). Similarly, nitrogen concentration is largely reduced whereas the amount of hydro-

gen becomes significant (higher than 5 at.%). As a result, a nearly amorphous oxynitride compound with a high oxygen content:  $\text{TiO}_{1.03}\text{N}_{0.76}\text{H}_{0.15}$  is deposited for  $P_{\text{H}_2\text{O}} = 1.5 \times 10^{-2}$  Pa. As water vapour pressure increases, a reverse evolution of oxygen and nitrogen atomic compositions is observed and hydrogen concentration

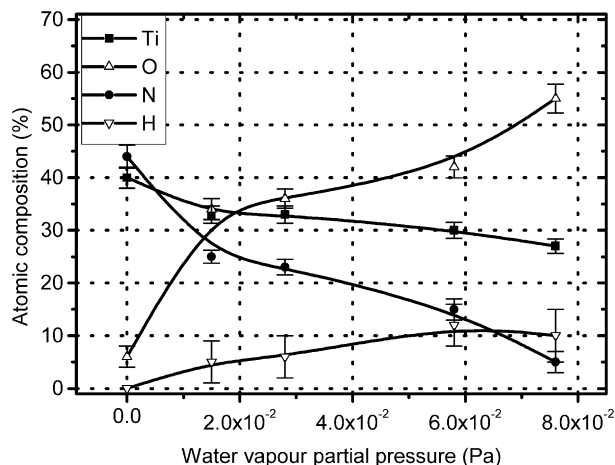


Fig. 6. Influence of the water vapour partial pressure on the chemical composition of titanium oxynitride thin films. A reverse evolution of oxygen and nitrogen concentrations can be noticed as well as an increase of hydrogen amount.

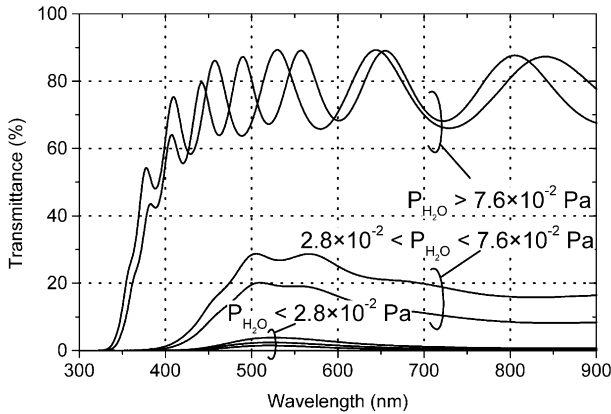


Fig. 7. Transmittance spectra of titanium oxynitrides deposited on glass substrate in the visible region. Films prepared with water vapour partial pressures lower than  $2.8 \times 10^{-2}$  Pa exhibit golden-orange metallic colours and are strongly absorbent whereas those obtained with pressures higher than  $7.6 \times 10^{-2}$  Pa are interferential. Intermediate water vapour partial pressures lead to compounds with irregular interference fringes and a moderate transmittance.

reaches 10 at.% for  $P_{\text{H}_2\text{O}} = 7.6 \times 10^{-2}$  Pa. For higher water vapour partial pressures, O/Ti ratio exceeds 2.0 and the deposited films tend to behave as titanium dioxide compounds ( $\text{TiO}_{2.04}\text{N}_{0.19}\text{H}_{0.37}$  for  $P_{\text{H}_2\text{O}} = 7.6 \times 10^{-2}$  Pa). Similar results were obtained by others [8,9,11,12,16,36] about the reverse evolution of oxygen and nitrogen concentrations in metallic oxynitride coatings by simple variation of the oxygen partial pressure. In addition, in spite of a very low supply of oxygen into the process (or low water vapour pressure in our case), an abrupt increase of the oxygen amount in oxynitride films is systematically measured mainly due to the strong reactivity of oxygen with metals.

### 3.3. Optical and electrical behaviours

The optical transmittance spectra of the film/glass substrate system measured in the visible region (300–900 nm) are shown in Fig. 7 as a function of the water vapour pressure. The spectra of TiN coatings and those deposited with low water vapour pressure ( $P_{\text{H}_2\text{O}} < 2.8 \times 10^{-2}$  Pa) are completely absorbent in the measured wavelength range. For moderated water vapour pressures ( $2.8 \times 10^{-2} < P_{\text{H}_2\text{O}} < 7.6 \times 10^{-2}$  Pa), the films are slightly transparent and exhibit a dark green colour aspect. Transmittance reaches a maximum close to 550 nm whereas absorption becomes significant for wavelengths higher than 800 nm. The strong absorption of titanium oxynitrides near 900 nm (1.38 eV) is not completely understood. Taking into account Vogelzang et al. investigations [37], one can suggest that it is closely linked to a resonance in the dielectric function at 1.2  $\mu\text{m}$ . The authors claimed that this resonance (located at 1.1 eV) might correspond with a weakly allowed transition of

Ti-3d electrons to O/N 2p levels. However, due to a lack of knowledge and the complexity of the electronic structure of the titanium oxynitride material, optical response of such coatings still remains an open question.

Beyond  $P_{\text{H}_2\text{O}} = 7.6 \times 10^{-2}$  Pa, the spectra display typical interferential fringes which supports that films prepared in this range of water vapour pressures behave as titanium dioxide. It is also worth to note that the absorption edge is shifted to lower wavelengths as the water vapour pressure increases. This blue shift commonly observed in transparent conducting oxides and usually attributed to the Bürrstein–Moss effect, correlates with the carrier concentration [38] and then, with the oxygen composition. For oxynitride compounds, further investigations are required because such compounds contain a significant amount of nitrogen.

Therefore, as previously reported in the results of the process characteristics (cf. Section 3.1), the optical properties of the films can be divided into three parts. For water vapour pressures lower than  $2 \times 10^{-2}$  Pa, properties of the coatings are similar to that of titanium nitride compounds with a notable amount of oxygen (TiN:O). Higher water vapour pressures ( $P_{\text{H}_2\text{O}} > 7.6 \times 10^{-2}$  Pa) lead to transparent  $\text{TiO}_2\text{:N}$  films and finally, for water vapour pressures included between  $2.8 \times 10^{-2}$  and  $7.6 \times 10^{-2}$  Pa, titanium oxynitride materials are obtained with optical properties which spread from metal to semiconductor.

Electrical conductivity measured at room temperature for various water vapour pressures (Fig. 8) and as a function of temperature (Fig. 9) corroborates with optical results and process analysis. Without water, titanium nitride films exhibit an electrical conductivity higher than  $10^4 \text{ S m}^{-1}$  at room temperature. As a small amount of water vapour is admitted into the sputtering chamber,

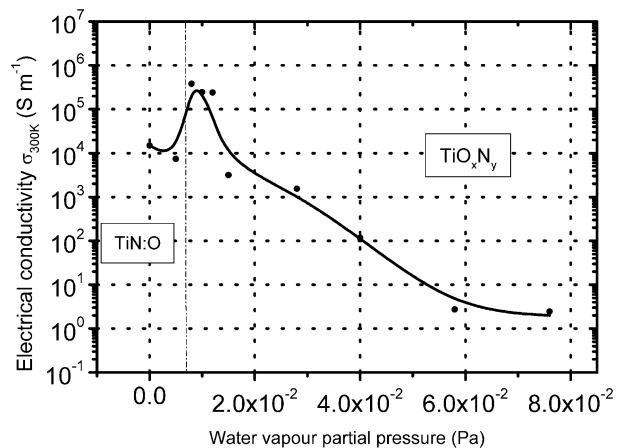


Fig. 8. Electrical conductivity  $\sigma$  at 300 K of titanium nitride and oxynitride thin films vs. water vapour partial pressure. Little supply of water vapour gradually changes the electrical properties of the films from metal to semiconductor.

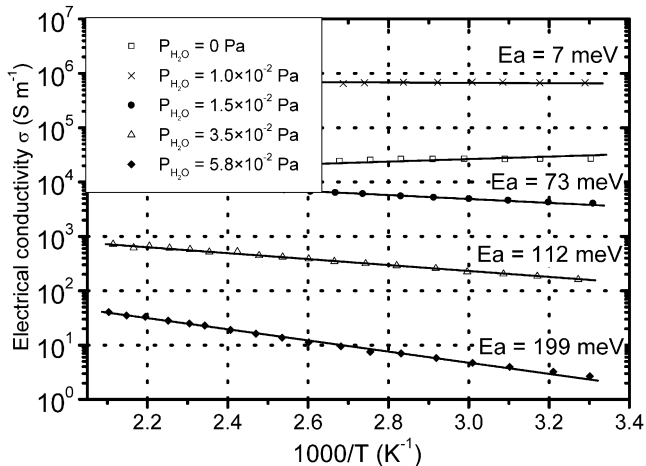


Fig. 9. Electrical conductivity  $\sigma$  vs.  $1000/T$  measured on titanium nitride ( $\square$ ) and oxynitride thin films for various water vapour partial pressures. The activation energy  $E_a$  (linear behaviour in the Arrhenius plot) is largely influenced by the water vapour partial pressure.

conductivity is weakly influenced and remains in the same order of magnitude. However, when the water vapour pressure is high enough ( $P_{\text{H}_2\text{O}} > 10^{-2}$  Pa), some process parameters like the target potential begin to increase as previously reported in Fig. 2. Similarly, electrical conductivity of the films is enhanced and reaches a maximum value  $\sigma_{300\text{ K}} = 3.8 \times 10^5 \text{ S m}^{-1}$  close to  $P_{\text{H}_2\text{O}} = 10^{-2}$  Pa. It also correlates with a large increase of the oxygen concentration in the films and with a colour change from orange brownish to a metallic dark green aspect. To the best of our knowledge, this surprising maximum of conductivity in titanium oxynitride thin films has never been observed. Commonly, a continuous decrease of  $\sigma$  is measured vs. oxygen supply in the process or oxygen concentration in the films [12,13,16]. In our case, this unusual evolution is not completely understood at the moment and should require further investigations. However, assuming that TiO and TiN phases with a very small crystal size (short range order from XRD results in Fig. 3) are both present in titanium oxynitride coatings prepared close to  $P_{\text{H}_2\text{O}} = 10^{-2}$  Pa, some titanium atoms are probably unbound with oxygen or nitrogen. Then, a mixture of substoichiometric  $\text{TiO}_{1-\delta}$  and  $\text{TiN}_{1-\epsilon}$  compounds are supposed to be formed in this range of water vapour pressures. Since electrical conductivity of TiO and TiN films is improved when metalloid concentration is decreased [35,39], one can suggest that such a mixture produces a synergetic effect of the electrical properties of oxynitride compounds.

As water vapour pressure increases from  $10^{-2}$  to  $7.6 \times 10^{-2}$  Pa, the electrical conductivity is monotonously reduced down to  $2.6 \text{ S m}^{-1}$ . It is related to the increasing oxygen content in the films since oxygen deficiency in oxide materials contributes to the intrinsic

electronic conductivity [40]. This remarkable drop of  $\sigma_{300\text{ K}}$  as a function of  $P_{\text{H}_2\text{O}}$  (five orders of magnitude) specially highlights the increasing semiconducting behaviour of the films with increasing the water vapour pressure and so, oxygen content. Electrical conductivity measured against temperature supports these results as displayed in Fig. 9. The metallic behaviour of TiN coatings (decrease of  $\sigma$  with temperature) prepared without water or with very low water pressure vanishes for water vapour pressures higher than  $10^{-2}$  Pa. A negative slope of  $\log \sigma = f(1000/T)$  is measured (linear behaviour in the Arrhenius plot), which increases up to  $E_a = 199 \text{ meV}$  as  $P_{\text{H}_2\text{O}}$  reaches  $5.8 \times 10^{-2}$  Pa. For  $P_{\text{H}_2\text{O}} \leq 1.5 \times 10^{-2}$  Pa, the negative slope still exhibits low values ( $E_a \leq 73 \text{ meV}$ ) indicating that titanium oxynitride thin films with low oxygen contents (lower than 32 at.%) are still partly metallic. A gradual transition from metallic to semiconducting behaviours is finally observed as water vapour pressure increases. This also corresponds to the reverse evolution of oxygen and nitrogen concentrations in the films. For higher water pressures, electrical resistivity becomes too much important to be measured by the four probes technique and the coatings tend to behave as titanium dioxide compounds (insulators).

As a result, the transition from metal to semiconductor of titanium oxynitride thin films is clearly demonstrated from optical and electrical measurements but at the moment, it is not obvious to provide a successful interpretation of such characteristic. Nevertheless, it may be related to the difference in ionicity between Ti–O and Ti–N bonds. Since ionicity in a single bond increases with the difference in values of electronegativity between two elements forming the single bond, it means that the Ti–O bond leads to a larger charge transfer than the Ti–N bond (electronegativity of O and N is 3.5 and 3.0, respectively). Supposing that titanium oxynitride films are formed by a mixture of Ti–O and Ti–N bonds and assuming that the amount of Ti–O bonds increases (whereas the amount of Ti–N bonds decreases) with water vapour pressure, the transition from metal to semiconductor can be ascribed to a larger ionicity of titanium oxynitrides as  $P_{\text{H}_2\text{O}}$  increases.

#### 4. Conclusion

Water vapour was successfully used as reactive gas to produce titanium oxynitride thin films by dc reactive sputtering. A systematic change of the water vapour partial pressure led to a monotonous and controlled evolution of the reactive sputtering process from nitrified to oxidised sputtering mode. Deposition rate and the state of the target surface estimated from measurements of the target potential exhibited a continuous variation as a function of the water vapour supply. Analysis of such experimental parameters allowed to determine three

types of operating conditions favourable to deposit titanium nitride (TiN:O), titanium oxide (TiO<sub>2</sub>:N) and titanium oxynitride thin films (TiO<sub>x</sub>N<sub>y</sub>) with various metalloids concentrations. The well-developed f.c.c. TiN phase was obtained for coatings prepared at room temperature and without or with low water vapour partial pressures. For higher water vapour partial pressures, sputter deposited titanium oxynitride and dioxide films exhibited poorly crystallised or amorphous structures. Optical and electrical characteristics of the films revealed a gradual transition from metallic to semiconducting behaviours as a function of the water vapour partial pressure. This transition was correlated with the reverse variation of the oxygen and nitrogen concentrations and it was attributed to the coexistence of Ti–O and Ti–N bonds in the films. A reverse evolution of the amount of Ti–O and Ti–N bonds as well as oxygen and nitrogen vacancies are supposed to generate the gradual metallic to semiconducting transition of titanium oxynitride thin films.

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