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Nitrogen pulsing to modify the properties of titanium nitride thin films sputter deposited

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TiN_x thin films were grown on (100) Si and glass substrates by dc reactive magnetron sputtering. A titanium target was sputtered in $Ar + N_2$ atmosphere using a pulsing flow rate of the nitrogen gas. A constant pulsing period was used for every deposition whereas the nitrogen injection time was changed. The systematic variation of the nitrogen injection time led to a gradual decrease of the deposition rate and to a controlled modulation of the chemical composition of the TiN_x films (x between 0 and 1.05). Analysis of the crystallographic structure by X-ray diffraction showed that both Ti and TiN phases coexisted and a change of the preferential orientation from (200) to (111) occurred. The electrical conductivity and colour measurements in the CIE-$L^*a^*b^*$ system of colourimetry were also performed and correlated with the evolution of the N/Ti ratio.

1. Introduction

Titanium nitride (TiN) has widely been employed in many industrial applications because of its high melting point, hardness, wear and corrosion resistance [1–4]. Many chemical and physical vapour deposition techniques have been implemented for the preparation of TiN thin films including chemical vapour deposition [5], reactive evaporation of Ti in N_2 or NH_3 ambient [6, 7] and reactive sputtering [8–12]. Among these techniques, reactive sputtering is of special interest because it is an industrial process applicable to large-area deposition and because high quality films can be achieved even at low substrate temperatures. However, the reactive mode is quite complex and usually exhibits non-linear hysteresis effects of process parameters such as target potential or reactive gas partial pressure. In order to prevent such instabilities, particular devices or feedback control systems or high pumping speed were developed [13–17]. These technical improvements allowed a better control of the reactive sputtering process and they extended the characteristics of the deposited films. To the best of our knowledge, Aronson *et al.* [18] were the first to propose a pulsing introduction of the nitrogen gas to prepare TiN coatings by reactive sputtering. Later, some authors applied a similar technique to prepare oxides, nitrides, oxynitrides thin films or multilayered materials by reactive sputtering [19–25]. These investigations showed that the gas pulsing technique is an attractive way not only to modify coatings properties, but also to minimize instabilities of the reactive sputtering process.

In the present work, we report on the properties of titanium nitride thin films prepared by reactive sputtering with a controlled pulsing flow rate of the reactive gas. Nitrogen was periodically injected into the chamber with a home made computer controlled modulation of the nitrogen mass flow rate. A rectangular wave function was used as a basic controlling signal with a constant period whereas the on and off times (t_{ON} and t_{OFF}, respectively) were systematically and oppositely changed. The influence of an increasing t_{ON} time on the process parameters, crystallographic structure, electrical conductivity and colours of the films were investigated and compared with the evolution of the N/Ti ratio.

2. Experimental details

TiN_x thin films were deposited onto (100) silicon wafers and glass substrates by dc reactive magnetron sputtering. A titanium metallic target (99.6%) was sputtered with a current density of the target $J_{Ti} = 100$ A m^{-2} in an $Ar + N_2$ gas mixture. The argon partial pressure was kept constant at 0.25 Pa during all depositions and the nitrogen mass flow rate was pulsed following a rectangular wave pattern (Fig. 1). Maximum and minimum nitrogen mass flow rates q_{N2M} and q_{N2m} were fixed at 0.50 and 0 sccm, respectively. The period T of the pulses was maintained constant at $T = 16$ s [23] whereas the t_{ON} time was systematically increased. The substrates were grounded and their temperature was maintained at 473 K for all depositions. The deposition time was adjusted in order to deposit films with the same thickness (close to 300 nm). The crystallographic structure of the films was determined by X-ray diffraction (XRD) in a grazing angle configuration ($\theta = 5°$) with Cu K_α monochromatised radiation. The chemical composition of the layers was

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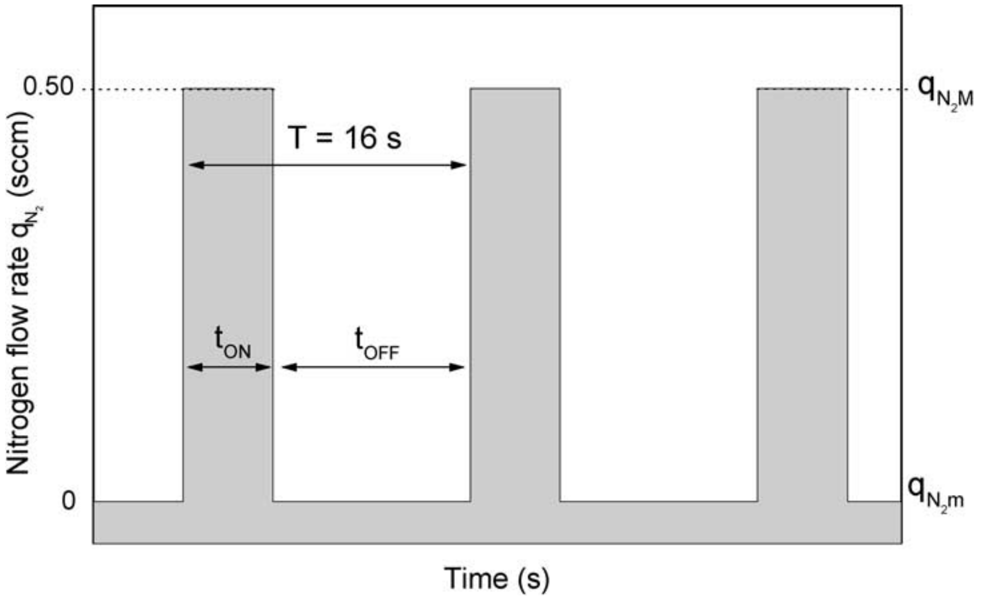

Figure 1 Schematic representation of the pulsing supply of the nitrogen mass flow rate. The pulsing period T was kept constant at 16 s whereas t_{ON} and t_{OFF} times have been systematically changed. Maximum and minimum nitrogen flow rates were fixed at $q_{N2M} = 0.50$ sccm and $q_{N2m} = 0$ sccm, respectively.

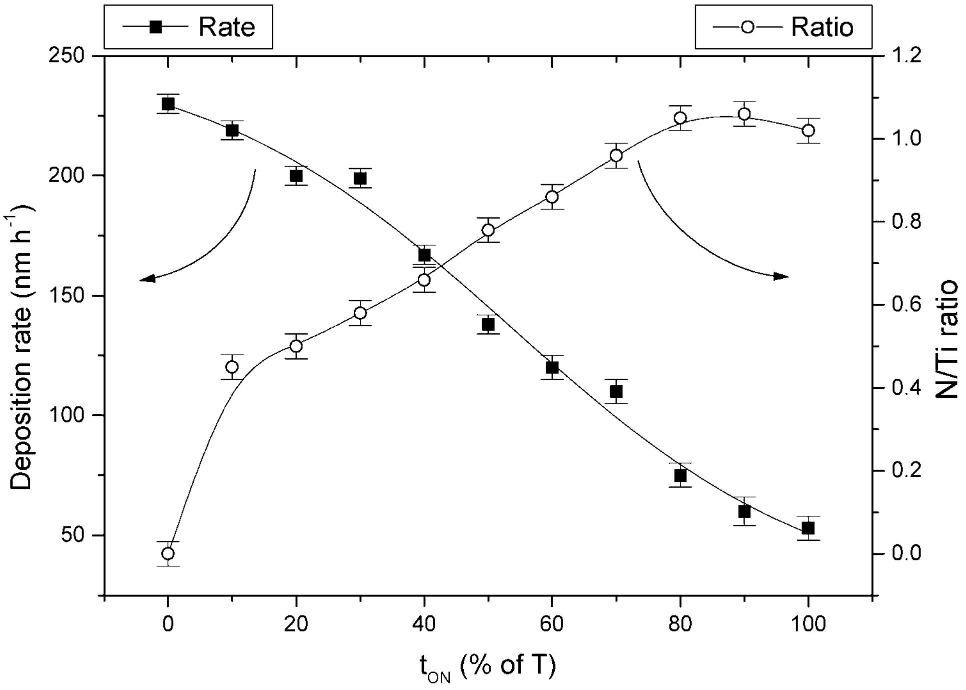

Figure 2 Continuous evolution of the deposition rate (■) and N/Ti ratio (○) as a function of the t_{ON} time. No abrupt transition of the deposition rate and ratio can be observed with the pulsing of the nitrogen gas.

obtained from electron probe microanalysis (EPMA) in the wavelength dispersion mode. The Cameca software "Strata" was used to minimize the overlapping effects between N K_α and Ti L1 lines. The electrical conductivity of the films deposited on glass substrates was measured at room temperature ($T = 300$ K) in the Van Der Pauw geometry. The colour of the films was quantified in the CIE-$L^*a^*b^*$ system of colourimetry. A Minolta CR-300 spectrometer was used to determine gloss L^*, a^* and b^* chromatic values.

3. Results and discussion

With a continuous supply of reactive gas, conventional reactive sputtering exhibits nonlinear and hysteresis effects of process parameters. A typical feature observed in the reactive mode is the sudden drop of the deposition rate and simultaneously, an abrupt increase of the metalloid concentration in the films [26–28]. With nitrogen pulsing, the deposition rate and the N/Ti ratio change monotonically as a function of the t_{ON} time (Fig. 2). The TiN_x deposition rate is reduced continuously from 230 down to 50 nm h^{-1} as the t_{ON} time increases from 0 to 100%. Similarly, chemical composition measurements reveal that various N/Ti ratios can be achieved by changing the t_{ON} time. As a result, the nitrogen pulsing flow rate leads to the deposition of sub-, over- or stoichiometric titanium nitride thin films ($0.45 \leq x \leq 1.05$ in TiN_x) whereas conventional reactive sputtering (constant supply of N_2) restricts the range of achievable metalloid compositions. Nearly stoichiometric TiN films are formed from $t_{ON} = 70\%$ with a deposition rate (100 nm h^{-1}) higher than those obtained with a constant supply of the nitrogen (50 nm h^{-1}). This result shows that the reactive gas pulsing technique enhances the deposition rate of stoichiometric titanium nitride compound (near 45% of the metallic rate) and supports previous investigations devoted to titanium oxide thin films [23, 24].

This well controlled and continuous evolution of the deposition rate and N/Ti ratio versus t_{ON} time is closely linked to the poisoning and cleaning phenomena on the surface of the target. From real time measurements of the Ti target potential U_{Ti} (Fig. 3), the state of the surface of the target can be assessed. During the t_{ON} time and for $t_{ON} = 10\%$, the potential suddenly increases from $U_{Ti} = 410$ to 428 V due to the nitridation of the surface of the target (compound sputtering mode). A titanium nitride layer (few nanometers thick) is formed on the surface of the target with a sputtering yield lower than that of titanium. Afterwards, U_{Ti} comes back to its original value (410 V) at the end of the t_{OFF} time. It means that a cleaning phenomenon of the target occurs during the t_{OFF} time (metallic sputtering mode). Up to $t_{ON} = 70\%$, the t_{OFF} time is long enough to restore the process to the metallic sputtering mode. In addition, the target potential exhibits a maximum of $U_{Ti} = 436$ V during the t_{OFF} time because of the removal of the titanium nitride layer on the surface of the target. At the moment, no clear explanation can be proposed for the maximum of the target potential. One can suggest that thickness and composition of the "poisoned" layer at the target have to be taken into account to describe fully the dynamic behaviour of the process. Finally, for t_{ON} higher than 80%, the t_{OFF} time is too short to remove the nitride layer on the surface of the target. The process is completely trapped in the compound sputtering mode. Thus, for $10 \leq t_{ON} \leq 70\%$, the reactive sputtering process alternates between metallic and compound sputtering modes. A titanium nitride layer with a low sputtering yield is formed on the surface of the target and sputtered during the t_{ON} time whereas this layer is removed and sputtering of titanium occurs in a second part of the t_{OFF} time. An increase of the t_{ON} time leads to a longer sputtering of titanium nitride compound, to a decrease of the deposition rate and then, to an increasing amount of nitrogen in the deposited films.

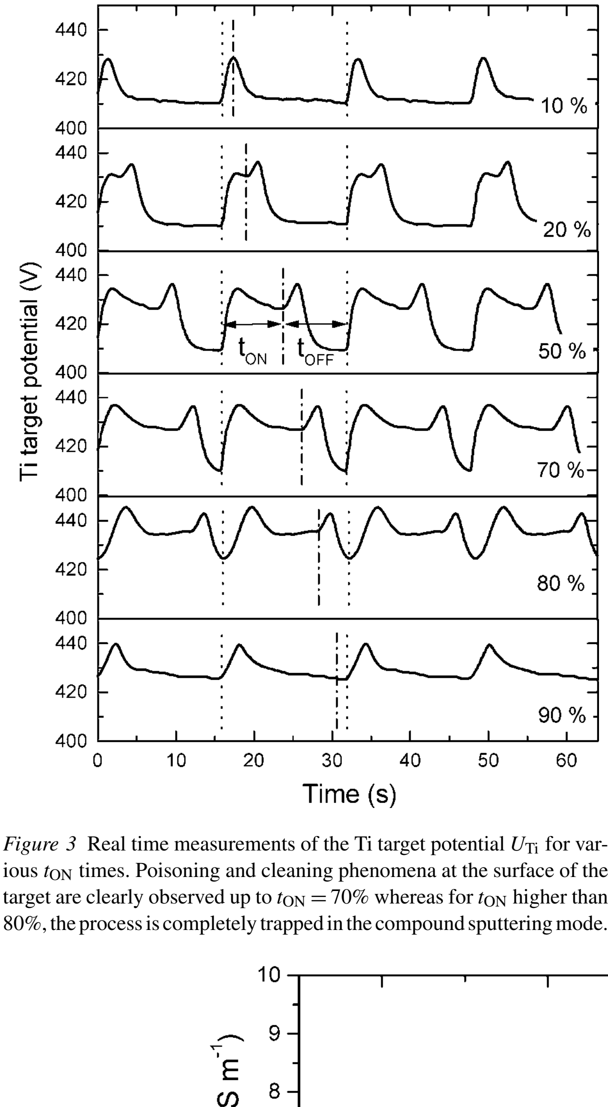

Figure 3 Real time measurements of the Ti target potential U_{Ti} for various t_{ON} times. Poisoning and cleaning phenomena at the surface of the target are clearly observed up to $t_{ON} = 70\%$ whereas for t_{ON} higher than 80%, the process is completely trapped in the compound sputtering mode.

The evolution of the N/Ti ratio can be correlated with the electrical conductivity measured at 300 K (Fig. 4). The conductivity σ exhibits a minimum ($\sigma = 3.0 \times 10^{-6}$ S m^{-1}) for $t_{ON} = 60\%$. In fact, these results are in a good agreement with that of Schiller *et al.*

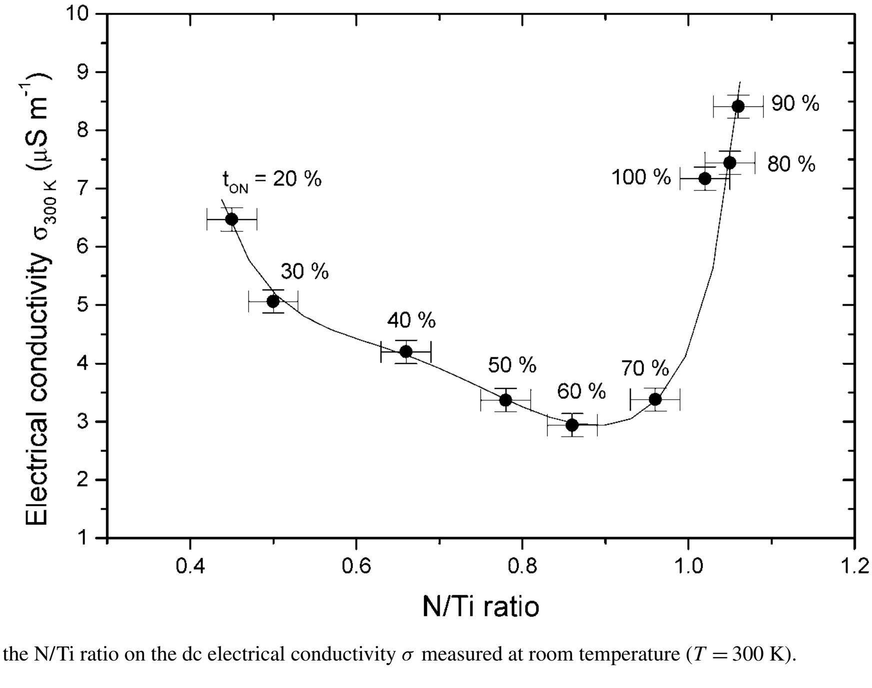

Figure 4 Influence of the N/Ti ratio on the dc electrical conductivity σ measured at room temperature ($T = 300$ K).

[29]. The authors have also investigated the electrical resistivity of titanium nitride thin films as a function of the N/Ti ratio. They similarly observed an optimum of the electrical properties of the layers for a ratio close to 0.6 for titanium nitride prepared by reactive triode sputtering, but no clear explanation was suggested. TiN_x prepared with t_{ON} included between 20 and 70% are sub-stoichiometric. For such films, the most significant defect is nitrogen vacancy, which returns one electron to the Fermi level and increases the free carrier concentration [30]. Then, the decrease of the electrical conductivity with the N/Ti ratio is closely linked to the reduction of the nitrogen vacancies as the t_{ON} time increases. For nitrogen-rich TiN_x films, the nitrogen atoms behave like nitrogen interstitials. Each defect captures one electron from the Fermi surface and decreases the free carrier concentration [30]. However, experimental measurements in Fig. 4 display a reverse evolution. An increase of the electrical conductivity is observed for over-stoichiometric thin films deposited with t_{ON} higher than 70%. No right answer can be proposed at the moment and this last result still remains an open question.

X-ray diffraction patterns of TiN_x films show that the crystalline structure is especially influenced by the t_{ON} time (Fig. 5). The hexagonal phase of metallic titanium is clearly observed without introducing nitrogen whereas Ti and TiN phases coexist when nitrogen is pulsed up to $t_{ON} = 10\%$. For t_{ON} higher than 20%, the hexagonal phase completely disappears and peaks related to fcc TiN phase are solely obtained. With an increase of the t_{ON} time, the crystallite size varies from 13.0 nm for $t_{ON} = 20\%$ to 23.0 nm for a continuous supply of nitrogen ($t_{ON} = 100\%$). It is also worth to note that a change of the preferential orientation from (200) to (111) direction occurs depending on t_{ON} (inset in Fig. 5). Until $t_{ON} = 10\%$, the occurrence of Ti and TiN phases mixture is mainly due to a growth competition between metallic and nitride phase which takes place on the growing film since the process alternates between the metallic and the compound sputtering mode (Fig. 3). An increase of the t_{ON} time favours the growth of polycrystalline TiN films. The preferential orientation of TiN films prepared for t_{ON} included between 20 and 100% originates from the impingement of metallic species on the film during the t_{OFF} time. Taking into account that the development of texture is often correlated with the channelling directions of particles in the crystal lattice and assuming that, according to Smidt [31] the ease of channelling is in the order (110), (200), (111), one can understand that changes of the TiN texture are due to a reduced flux of metallic species on the growing film as t_{ON} increases from 20 to 100%.

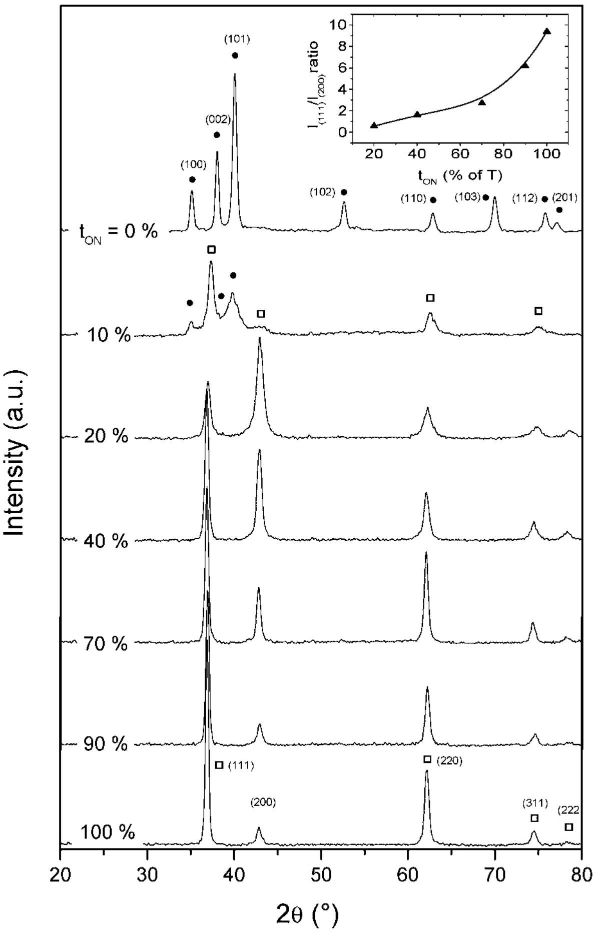

Figure 5 Grazing incidence ($\theta = 5°$) X-ray diffraction patterns of TiN_x thin films sputter deposited at 473 K and for various t_{ON} times (● = Ti; □ = TiN).

The group IVb nitrides have generated a great deal of interest because of their mechanical properties and their gold-like colours [32–35]. The typical colour of the nitrides and their metallic lustre are related to electron transition in the energy band. These electrons (on relaxation) emit yellow gold light and their number is a measure of brightness [32]. Colourimetric measurements based on the CIE-$L^*a^*b^*$ space colours have been carried out as a function of the t_{ON} time (Fig. 6). Titanium nitride thin films prepared with t_{ON} lower than 40% exhibit a silver-grey appearance in the reflection mode. For t_{ON} included between 40 and 70%, human colour perception of the films changes from metallic to the standard colour of yellow gold. With quantitative measurements of the colour, this is characterised by an abrupt decrease of the gloss L^* value from $L^* = 59$ to 45 a.u. as t_{ON} changes from 40 to 70% (Fig. 6a). In addition, it corresponds to large variations of chromatic values a^* and b^* (Fig. 6b). This typical evolution of the gloss L^* as a function of the t_{ON} time can also be correlated with that of the nitrogen concentration. From results in Fig. 2, any sub-stoichiometric $TiN_{1-\delta}$ is prepared for t_{ON} lower than 70% whereas nitrogen-rich $TiN_{1+\varepsilon}$ is obtained for t_{ON} higher than 70%. This t_{ON} time range corresponds to the formation of dark yellow–orange titanium nitride films exhibiting gloss L^* values lower than $L^* = 45$ a.u.

These colour changes agree with Schiller *et al.* results [29]. The authors studied the evolution of the visual colour perception of titanium nitride thin films as a function of the N/Ti ratio. TiN_x colours vary from titanium grey up to bronze as x value increases from 0 to 1. Similarly, Roquiny *et al.* [36] controlled the colour of titanium nitride coatings sputter deposited with a classical modification of the nitrogen mass flow rate and with a high pumping speed. The authors observed an abrupt decrease of gloss L^* and a typical loop curve

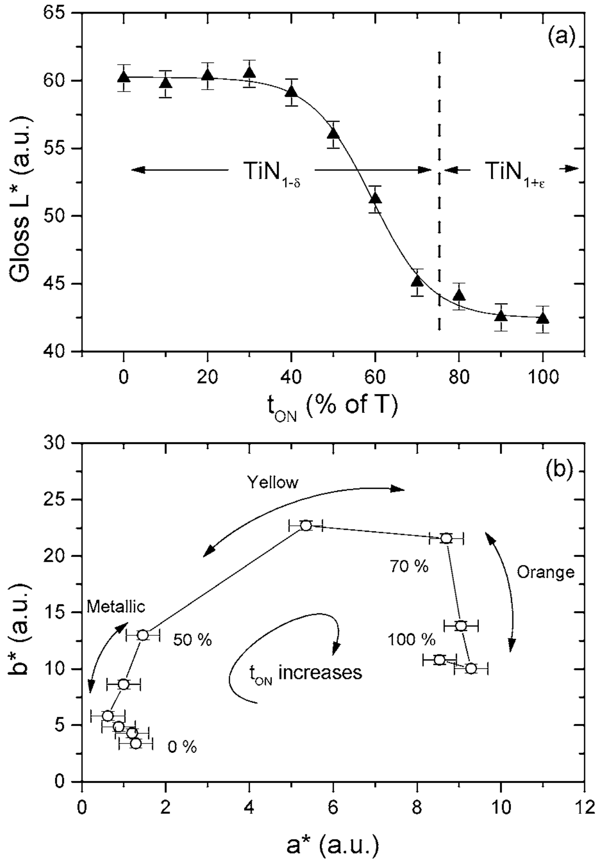

Figure 6 Evolution of gloss L^* (a) and chromatic dimensions a^* and b^* (b) as a function of the t_{ON} time. Reference colours: Fe: $a^* = 0.60$ a.u.; $b^* = 2.5$ a.u. Au (24 ct.): $a^* = 13$ a.u.; $b^* = 43$ a.u.

in the (a^*; b^*) chromatic diagram as the nitrogen mass flow rate increases. Our results presented in Fig. 6 are in good agreement with that of Roquiny *et al.* However, the drop of the gloss L^* value is widened and the spreading of the loop curve in the (a^*; b^*) chromatic diagram is improved with the nitrogen gas pulsing. These results support again that the pulsing technique is also a valuable method to modify colour properties of titanium nitride thin films for decorative applications.

4. Conclusion

The reactive gas pulsing technique was successfully used to prepare titanium nitride thin films by dc reactive magnetron sputtering. Nitrogen mass flow rate was pulsed in time following a rectangular wave pattern with a systematic variation of the t_{ON} injection time and a constant period $T = t_{ON} + t_{OFF}$. An accurate control of the t_{ON} and t_{OFF} times led to an enhancement of the deposition rate of stoichiometric titanium nitride thin films (about 45% of the metallic rate) with regard to conventional reactive sputtering. Any N/Ti ratio was achieved with this pulsing technique by modulating the reactive process between metallic and compound sputtering modes. The electrical properties as well as the crystallographic structure were also changed against the t_{ON} time. The well developed hc Ti phase or a mixture of Ti and TiN phases was achieved for the shortest t_{ON} times whereas an increase of the t_{ON} time favoured textured TiN films. Furthermore, the nitrogen pulsing technique appears as an attractive way not solely to modify the properties of the coatings but also to control the colour of decorative titanium nitride compounds from metallic grey to gold and finally brownish red.

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