Microstructural and elasto-plastic material parameters identification by inverse finite elements method of $Ti_{(1-x)}$ Al_x N (0 < x < 1) sputtered thin films from Berkovich nano-indentation experiments

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ABSTRACT

The mechanical properties of Ti_{1-x} Al_x N (0 < x < 1) films of different thicknesses deposited by r.f. reactive magnetron sputtering on Si < 100 > and high speed steel substrates have been investigated. The as-deposited coatings have been characterized by X-ray diffraction, atomic force microscopy, four-probe electric resistivity method, mechanical deflection of cantilever beams and Berkovich nano-indentation tests associated with inverse finite elements analysis. The coatings with x < 0.58-0.59 present cubic structure whereas for x > 0.7 a hexagonal structure is observed. Between these two compositions cubic and hexagonal structures coexist. The roughness depends on the films thickness and on the Al content and a minimum associated to a very fine microstructure is clearly observed in the two-phase coatings. The electric resistivity sharply increases as soon as hcp structure appears (x~0.6). The mean residual stresses are compressive, excepted for the AlN coating, and present a minimum at the neighborhood of x ~ 0.64 where a mixed structure is observed.

The indentation modulus $M_{<hkl>}$ and the Berkovich hardness $H_{B<hkl>}$ greatly depend on the Al content and a progressive decreasing has been observed for 0.58 < x < 0.7. For the $M_{<hkl>}$

evolution, a simple model taking into account the stiffnesses coefficients of TiN and AlN structures, the mean residual stress level and the variations of the lattice parameters in the two structure domains is proposed.

Knowing the elastic properties of these films, inverse finite elements analysis of the indentation curves considering a simple isotropic linear elasto-plastic behavior allows, as a function of the composition, the yield stress σ_Y and the linear hardening coefficient H_p^* to be estimated. σ_Y and H_p^* are in the ranges 4.2 to 6.8 GPa and 60 to 400 GPa, respectively. The maximum value of H_p^* / σ_Y which characterizes the ability of these coatings to exhibit plastic strain hardening is maximum for x= 0.5 and 0.6. The quality of the estimation was discussed through a practical identifiability study and quantified using an identifiability index. Tip radius and elasticity of the Berkovich indenter are two very relevant parameters to improve identifiability and correctly extract the plastic parameters of the behavior law. Scratch crack propagation resistance shows a evolution similar to those of H_p^* / σ_Y.

1 – Introduction

Among the metallic nitride used as protective coatings in order to improve the mechanical resistance of steel surfaces for various machining applications, Titanium and Aluminum nitrides have extensively been studied [1-3] and can be considered as model system. Hence, Ti_{1-x} Al_xN ternary nitrides crystallize in the NaCl cubic structure (fcc) for the low Al contents and in the ZnS hexagonal Wurtzite structure (hcp) for the high Al contents. The transition between these two structures occurs around x = 0.65 depending on the elaboration conditions [2-8]. The hardness of Ti_{1-x} Al_x N thin films increases with increasing Al content up to about the transition content and then a rapid decrease is observed [4-6], [9]. This is due to the structural decomposition and the formation of a mixed structure (fcc + hcp). Moreover, the replacement of Ti atoms by Al atoms increases the oxidation resistance at elevated temperature [2-4]. Therefore, the best mechanical properties combined to the best resistance to oxidation is obtained for the maximum Al content substituted to Ti in the fcc structure. However, recent studies [6-7], [10-12] show that the micro and nano structures of films are much more complex. The low solubility of Ti atoms in hexagonal structure gives rise to segregation between Al-rich hexagonal domains and Ti-rich grain boundaries when the Al

content exceeds 0.5 in the ternary system. Note that the role of this phase segregation under thermal treatments on the wear resistance has also been evidenced [3], [6-7], [10].

In our previous papers [8], [11-13], the structures at different scales (macro, micro and nano) of $Ti_{1-x}Al_x$ N films elaborated by physical vapor deposition radio-frequency sputtering have extensively been studied by X-ray diffraction (XRD), X-ray absorption fine structure (EXAFS) performed at both Al and Ti K edges, scanning and transmission microscopies (SEM and TEM). As a complement of these different papers the present investigation focuses on the mechanical properties of such deposited films. Hence, with respect to the Al content ($0 < x < 1$), the different $Ti_{1-x}Al_xN$ films deposited on Si and steel substrates were examined by X-ray diffraction to determine the microstructure parameters (growth directions, lattice parameters, FWHM (Full Width at Half Maximum) of diffraction peaks), by atomic force microscopy (AFM) to measure the root mean square roughness ($R_{ms)}$ and the morphology of the surface of the films, by four-probe electrical resistivity method, by mechanical deflection of cantilever beams to estimate the mean internal stress and by nano-indentation to determine the indentation modulus and the hardness of the films. The plastic deformation parameters (yield stress σ_y and work hardening coefficient H^*_p) will be determined for each Al content by inverse finite elements method of the indentation curves. The quality of the estimations will be discussed through a practical identifiability study and quantified using an identifiability index.. Note that the quantification of these two parameters has never been reported in the literature.

2 – Experimental procedures

2.1 Sample fabrication

Titanium aluminum nitride $Ti_{1-x}Al_xN$ films have been deposited by radio frequency magnetron reactive sputtering in Ar-N_2 reactive mixture from a composite metallic target [14] onto both Si (100) and stainless steel substrates [8], [14]. The steel substrates come from a thick plate made of high speed steel (X90WMoCrV6.5-4.2) which is commonly used in cutting tool manufacturing. After machining the blocks have been quenched and polished. Target materials (diameter ~ 50 mm) were made from metallic titanium and aluminum and powered by a rf generator (13.56 MHz) at 80 W. The target was divided into 12 even parts in order to change the $S_{Al} / (S_{Al} + S_{Ti})$ area ratio allowing the adjustment of the (x) Al content [14]. Thus seven compositions ($0 < x < 1$) have been elaborated (Table I). The substrate holder was water cooled at T_s = 298 K. The substrates have been cleaned with acetone and

alcohol and pre-sputtered in pure Ar atmosphere with a negative bias voltage of -220 V for 40 min. The pressure reached before the introduction of the gas was 10^{-5} Pa and the Ar and N_2 mass flow rates were controlled and adjusted to keep a constant total sputtering pressure of 0.65 Pa. The Ar pressure was kept constant at 0.55 Pa using a mass flow rate controller and a constant pumping rate of 10 Ls^{-1}. The N_2 pressure was fixed at 0.1 Pa to run the process in the nitrided sputtering mode. More details on the deposition parameters are given in refs. [8][11].
With these experimental conditions and as reported in Table I, the growth rate V_d is an increasing function of the Al content. V_d increases from about 200 nmh^{-1} for TiN to about 680 nmh^{-1} for the AlN. According to the characterization methods, the deposition time has been adjusted in order to prepare three sets of films: thinner films of about 0.3 µm for XRD analysis, films of about 1 µm thick for the stress analysis and the AFM measurements and thicker films of about 3 µm for the nano-indentation experiments and the AFM measurements. Table I gives the exact values of the film thicknesses with respect to the composition and the nature of the substrate. The composition of the specimens has been determined from an energy dispersive spectrometer and the Al content is higher that the one given by the $S_{Al}/S_{Al}+S_{Ti}$ area ratio as shown by Rauch et al. [14] (Table I).

2.2 Experimental methods

The crystallographic structure of the films has been investigated by using a Panalytical X'pert PRO diffractometer equipped with a prefix hybrid device and the Cu $K\alpha_1$ radiation (λ = 0.154 nm). The X-ray diffraction patterns have been recorded at room temperature in $\omega/2\theta$ parallel beam geometry with ω = 10°. A real time multiple strip-type detector has been used and the accumulation lasted about 900 s per step of 0.17°.
The exact thickness e_f of the films (Table I) has been measured with a stylus surface profiler DEKTAC 3030.
The electric resistivity has been measured by the classic four-probe method at room temperature.
Si(100) cantilever structures correspond to a display with seven single beams of 0.5 mm width and different lengths in the range of 0.5 to 3.5 nm. This display allows us to measure with an optical microscope the deflection at the extremity of the beams due to the mean residual stress into the sputtered film. Note that the thickness e_s of the Si beams has been determined by a direct observation of the cross section thanks to a scanning electronic microscope (SEM JEOL 2100FCs); $12 < e_s < 16$ µm.

The surface morphology and the R_{ms} (root mean square) roughness of the films have been investigated with an atomic force microscope (AFM – PSIA XE 150) in a non-contact mode. Different areas of 1 x 1 μm^2 and 4 x 4 μm^2 were scanned at three different positions in the surface in order to make sure that the images and the roughness taken in AFM are representative of the film surface.

Some TEM observations of the cross section of the films after focused ion beam milling (Philips FIB 200) have been realized.

Nano-indentation tests have been performed on the $Ti_{1-x}Al_xN$ films of 3 µm thick using a nano-indenter II^s (Nano-Instrument) with a Berkovich tip. To accurately determine the elasto-plastic properties of the deposited films thanks to inverse finite elements modeling a blunt Berkovich tip with a R radius of 550 ± 50 nm has been used [15-25]. Indeed, as further shown, the tip radius and the deformability of the indenter are very important parameters to accurately determine the inelastic properties of thin films thanks to inverse identification of nano-indentation curves. Note that, for a perfect self similar Berkovich tip (R<100 nm) only one point of the stress-strain curve could be identified [15-20]. The study was conducted following the continuous contact stiffness measurement procedure (CSM) [26] with a frequency of 45 Hz and an indenter vibration amplitude of 1 nm during the penetration of the tip into the sample. For each tested film the measurement sequence consists on 6 indents with a 50 µm space between them on three or four different zones of the film (18 or 24 indents), with a maximum load of P_{max} = 160 mN. The penetration speed was not constant but increased with depth from 0.3 to 2.1 mNs^{-1}. Note that some complementary experiments have also been carried out using a CSM-NHT instrument equipped with a Berkovich tip. In this case the tip radius of the indenter is of the order of 100 ± 20 nm.

3 – Structural and electrical characterizations of the films

3.1 X-ray diffraction analysis

The diffraction patterns of these thin films (e_f ~ 300 nm) deposited on Si substrate have already been presented in the paper of Tuilier et al. [11]. From the 2θ values of the maximum of the diffraction peaks and the full width half maximum (FWHM) values Δ2θ of these peaks, the growth directions, the lattice parameters (Bragg's formula) and the structural domain size (Scherrer's formula) have respectively been deduced [27]. As a function of the Al content, Fig. 1 summarizes the evolution of the lattice parameters (a_c: lattice parameter of the cubic

NaCl-type crystal, a_h and c_h: lattice parameters along the $\vec{a}$ and the $\vec{c}$ axis of the hexagonal wurtzite-type crystal) deduced from the position 2θ of the diffraction peaks. TiN exhibits a single large peak centered on $2\theta = 42.3 \pm 0.08°$ (thus $a_{c(200)} = \lambda / \sin\theta = 4.27 \pm 0.01$ Å) corresponding to the [200] direction of the NaCl-type crystal structure. The $a_{c(200)}$ value is slightly higher than the tabulated one for powder samples [28]: $a_{c0} = 4.24$ Å. This indicates that the TiN film exhibits a compressive residual stress state which will be further quantified (section 4.1). For Ti-rich films (x = 0.38 and 0.5) an additional diffraction peak at 2θ = 36.9°, narrower than the [200] one appears. This peak approximately corresponds to the 2θ value of the <111> diffraction planes which is positioned at 2θ = 36.1° in unstressed TiN crystal. The lattice parameters $a_{c(200)}$ and $a_{c(111)}$ ($a_{c<111>} = \lambda\sqrt{3}/2\sin\theta$) are slightly different and lower than the one of the TiN film (Fig. 1). Moreover, the [111] peak has a narrower FWHM than the [200] one. These two points indicate a nanostructuration within the films with domains more or less stressed depending on the growth direction. AlN and Al-rich film (x = 0.86) patterns reveal a single narrow peak at $2\theta = 35.95 \pm 0.05°$ and $36.02 \pm 0.05°$ respectively, indicating a preferential growth along the $\vec{c}$ axis of the hexagonal Wurtzite lattice. The deduced lattice parameters $c_{h(002)}$ ($c_{h(002)}=\lambda/\sin\theta$) and $a_{h(002)}$ are reported in Fig. 1 and such that $(c_h/a_h)_{(002)} = 1.60 \pm 0.001$. Contrary to TiN film the lattice parameters of the AlN film ($a_{h(002)} = 3.12 \pm 0.01$ Å, $c_{h(002)} = 4.99 \pm 0.01$ Å) are consistent with a free stress growth ($a_{h0} = 3.11(1)$ Å and $c_{h0} = 4.98(1)$ Å, respectively [28]). This point will be further confirmed (section 4.1). The narrowness of the (002) peaks shows the good crystalline quality of these films. For the intermediate compositions (x = 0.6 and 0.68) a distorted hexagonal structure is highlighted. The (002) reflection is shifted toward the low 2θ values (34.45° and 34.84°, respectively) and an additional peak at 2θ = 32.15° assigned to the (100) reflection is equally observed. The peaks are significantly broadened with respect to the AlN and $Ti_{0.14}Al_{0.86}N$ films. The large lattice parameters increase suggests an incorporation of Ti atoms in the hexagonal structure [11]. Moreover, an increase of the background centered at about 2θ = 37° reveals a weak contribution of the (111) oriented cubic domains. Indeed, as shown by Tuilier at al. [11] for x = 0.68 (Al K-edge EXAFS and XRD), hexagonal domains have grown while at the grain boundaries disordered cubic Ti rich clusters has been formed.

3.2 AFM measurements

The R_{ms} root mean square roughness and the surface morphology of the different films of about 1 µm and 3µm thick have been investigated on 1 x 1 μm^2 and 4 x 4 μm^2 areas. A very fine structure in agreement with the columnar growth of this kind of deposit has been observed [13]. Moreover, a coarse-grained structure appears with the increase of the Al content. However, as shown in Table I, the thickness of the films is not constant but increases with the Al content and the principal change in the surface morphology could be attributed to the rise of the column diameter with the film thickness which is a common property of the growth of sputtered films. The surface morphology on 1 x 1 μm^2 area of 3 µm thick films exhibits very coarse grains, excepted for x = 0.6, which shows that the column diameter greatly increases with the film thickness. Fig. 2a shows, as a function of the Al content, the evolution of the R_{ms} roughness for different scan areas: 0.25 x 0.25 μm^2, 1 x 1 μm^2 and 4 x 4 μm^2 for the 1 µm thick films. For these films the 1x1 μm^2 and 4 x 4 μm^2 areas give the same R_{ms}. R_{ms} is of the order of 2.5-3 nm in the fcc domain and of 3.5 nm in the hcp domain, in a qualitative accordance with the AFM surfaces morphologies. For x = 0.6, in the fcc + hcp range a very small roughness of about 1 nm is measured. Over very small scan area, 0.25 x 0.25 μm^2, excepted for x = 0 and 0.6 where a very fine surface morphology can be observed and consequently R_{ms} is independent of the scan area, the roughness is smaller than for the 1 x 1 μm^2 area. Indeed, at this scale and as it can be observed on the AFM pictures a very fine microstructure can be evidenced. For the 3 µm thick films, on 4 x 4 μm^2 scan area, the roughnesses are greater than those measured on 1 µm thick films and also present a minimum in the fcc + hcp range. Hence, R_{ms} is an increasing function of the film thickness. Note that, the standard deviations of the nano-indentation measures are directly related to the R_{ms} parameter, as further described in (4.2.1.1).

The mean column diameter at the surface of the films can be evaluated from the AFM pictures. This has been done on the 1 x 1 μm^2 and 0.25 x 0.25 μm^2 areas for the 1 µm thick films and the results are presented in Fig. 2b: the mean column diameter ϕ is plotted as a function of the Al content. Moreover, for the 0.3 µm thick films (XRD, Table I) the structural domain size (or the nano-crystal size) d* was calculated from the FWHM of the diffraction peaks using the Scherrer's formula. The results are given in Fig. 2b and it is shown that the evolutions of ϕ (1 x 1 μm^2) and d* are parallel and present two maxima for x = 0.5 and 0.86 in the fcc and the hcp domains, respectively. Of course the ϕ and d* values are different. This is

due to the application domain of the Scherrer's formula which is not entirely verified in the present case and to the difference in the film thicknesses.

However, the values of the diameters of the very fine crystallite structures determined on the 0.25 x 0.25 μm^2 areas are close to those of d* and in the range 5 to 40 nm. This is in agreement with the HRTEM results reported by Girleanu et al. [13] on the same films: d* is in the 5-30 nm range. The ϕ and d* values in the hcp domain are higher than those in the fcc domain and present a minimum in the fcc + hcp region. This evolution is consistent to the one observed on the roughness (Fig. 2a). The values of the column diameters ϕ (1 x 1 μm^2) are in the range 60-80 nm in the fcc domain and 80-120 nm in the hcp region. These values are close to those obtained by TEM direct imaging after FIB sectioning of 1.2 µm thick films: ϕ = 80 nm for TiN and $Ti_{0,5}Al_{0,5}N$, and ϕ = 60 nm for $Ti_{0,14}Al_{0,86}N$ (Fig.2b).

3.3 Electric resistivity of the films

The electric resistivity of the films deposited on the Si substrate was measured at room temperature on two or three different zones. The results are given in Fig.3. Note that TiN conducts electricity like a metal but that AlN is a good insulator. Hence, the electric resistivity slowly increases with the Al concentration in the bcc structure (conductor), but as soon as a small amount of hcp structure (insulator) appears (x > 0.58-0.59, see Fig.1) the resistivity sharply increases from about 66 10^{-4} Ωcm for x = 0.5 to 460-600 10^{-4} Ωcm for x = 0.6. For x > 0.6 the electric resistivity cannot be determined with our experimental device.

4 – Mechanical characterization of the films

4.1 Mean residual stress measurements

The analysis of the bending of the bilayer cantilevers (Si substrate + films, Table I) as a function of the Al content gave valuable informations about the mean stress levels in the film. Note that the nano-indentation results (indentation modulus and hardness) are directly affected by the mean stress level. This will be further quantified (4.2). For a given display corresponding to a fixed Al content the deflections δ_m at the extremity of the seven cantilevers of different lengths L (0.5 mm to 3.5 mm by step of 0.5 mm and a width of 0.5 mm) have been measured thanks to optical microscope.

Several theoretical models regarding stress analysis of single layer of thin film deposited on an elastically isotropic substrate have been developed since the first works of Stoney in 1909

[29-32]. The first order development of the general solution gives a generalized writing of the Stoney's equation:

$$\sigma_0 = \frac{E_s e_s^2 \delta_m}{3(1-\nu) e_f L^2} \left(1 + 4 \frac{E_f e_f}{E_s e_s} + \varepsilon_{(0)} \right) \quad (1)$$

Note that in this study, the use of the Stoney's equation (first term in Eq.(1)) would have introduced a significant under-estimation of the stress in the film since the value of the term $\left(1 + 4 \frac{E_f e_f}{E_s e_s} \right)$ is in the range of 1.5 to 2.2. The E_f values have been determined from the nano-indention tests on the different films (see below) and E_s=165 GPa. Following the Eq.(1) the representations $\delta_m = f(L^2)$ (Fig. 4) should be linear and the slope of each straight line permits the mean stress σ_0 to be determined. All the films present a compressive stress state excepted for the AlN film which is in a tensile one (Fig.4). Figure 5 gives, as a function of the Al content, the evolution of the mean residual stress. Some results obtained in previous unpublished work have also been reported. In the fcc area the stress weakly decreases from -2.7 GPa to -2 GPa with the Al content which is in agreement with the results reported in the literature [4] [7]. On the contrary, in the hcp domain the stress greatly evolves from -1.9 GPa for x = 0.86 to +0.5 GPa for x = 1. In the intermediate domain where the two phases coexist the stress values are relatively low of the order of -0.8 GPa for x = 0.6. A minimum value close to zero could be expected for x ~ 0.64-0.66. Hence, the stress variation presents a very significant minimum in the fcc + hcp region. As shown in Figs 2a-b, the roughness and the estimated superficial mean column diameter ϕ also present a minimum in the vicinity of x = 0.64. The low residual stress values could be attributed to the stress relaxation due to the grain boundaries sliding of the un-deformable small grains. This is supported, as previously mentioned, by the Al K-edge EXAFS measurements reported by Tuilier et al. [11] which show that grain boundaries of disordered cubic Ti rich clusters has been formed for x = 0.68.
Note that for TiN and AlN films the mean stress levels (compressive and slightly tensile, respectively), are in quantitative agreement with the shifts of the XRD peaks.

4.2 Nano-indentation results

As mentioned in appendix A1, nano-indentation tests allow the indentation modulus $M_{<hkl>}$ and the Berkovich hardness $H_{B<hkl>}$ to be determined. These two quantities depend on the direction <hkl> of the domain growth.

4.2.1.1 Indentation modulus $M_{<hkl>}$:

Figure 6a represent for each tested Al content the evolution of the mean measured values (18 or 24 indents) of the indentation modulus $M_{<hkl>meas}$ versus the reduced indentation depth h/e_f. As the indentation modulus of the Si substrate ($M_S=M_{Si}$ ~173 GPa, Table II) is lower than those of the TiAlN films, due to the substrate effect, the measured indentation moduli continuously decrease with h/e_f. Moreover, for h/e_f < 3 %, due to the spherical shape of the Berkovich indenter tip (R~550 nm), the $M_{<hkl>meas}$ moduli are increasing functions of the penetration depth [33]. The true modulus of the films can be obtained by extrapolating the measured values in the neighbourhood of h/e_f = 0. Among the numerous analytical expressions to take the substrate effect into account [33-36], the King's model [34] has been used as the indentation modulus $M_{<hkl>}$ of the film is the only one unknown in this model. Hence, the measured indentation modulus $M_{<hkl>meas}$ is given by:

$$M_{<hkl>meas} = \left[\frac{1}{M_{<hkl>}} + \left(\frac{1}{M_S} - \frac{1}{M_{<hkl>}} \right) \exp - \frac{\alpha e_f}{\sqrt{A_c}} \right]^{-1} \quad \text{with} \quad A_c = 24{,}56\, h_c^2 + \sum_n a_n \qquad (2a)$$

.

α is a parameter which depends on the projected contact area and for a triangular Berkovich indenter, [34] :

$$\alpha \approx \frac{1}{2} + \frac{3}{4} \left(\frac{\sqrt{A_c}}{e_f} \right)^{1/2} \qquad (2b)$$

$M_{<hkl>}$ and M_S are the indentation moduli of the film and the substrate, respectively.

The King's model predictions over the entire h/e_f range have been plotted in Fig.6a. From these predictions the true indentation modulus without substrate effect (horizontal part of the curves) is obtained for h/e_f < 2%, thus for h< 60 nm. The values for h = 0 have been reported in Fig.6b and correspond to those of the indentation modulus of the films. The three domains highlighted by the XRD analysis (section 3.1) are perfectly identified. The value determined for x = 0.5 with the steel substrate is close to the one measured with the Si substrate. Note that the results obtained by linear extrapolation to h = 0 of the curves of Fig. 6a (linearization on the range h/e_f = 3.3 to 6.6 %) are also reported in Fig. 6b. In the fcc domain $M_{<hkl>}$ is in the

range 400-440 GPa, in the range 300-340 GPa for the hcp domain and of the order of 240-380 GPa in the fcc + hcp region for x = 0.6 to 0.68. As a comparison, the Kutschej et al. [6] results have also been plotted in this figure and are in a fairly good agreement with those of the present study. This point will be further discussed in the paper. From a quantitative point of view and as mentioned in appendix A1, knowing the stiffness coefficients C_{ij} of TiN and AlN, the indentation modulus for a given direction can be calculated. TiN is weakly anisotropic [37] and the C_{ij} values taken into account [38-39] are listed in Table II. The values M_{iso} and ν_{iso} of isotropic film and evaluated thanks to the Hashin and Shtrickman formulation [40] have also been reported in Table II. Applying the Eq.(A1-6) [41] for the growth directions of the TiN film the values of $M_{<100>}$ = 450 GPa and $M_{<111>}$ = 440 GPa are obtained. Experimentally, a value of M = 400 ± 20 GPa has been determined, thus weakly lower than the theoretical one. However, this can be attributed to the poor crystallinity of the TiN films as observed on the X ray diffraction patterns [11]. The films with x = 0.38 and 0.5 which present a good crystallinity [11] exhibit an indentation modulus of 430 GPa and 440 GPa, respectively. These values are in a fairly good quantitative agreement with the theoretical one (Table II), especially for the <111> direction which has been identified as a growth direction (Fig. 1).

For the AlN, the C_{ij} coefficients of sputtered thin films [42] are listed in Table II. As previously done, the application of Eq.(A1-7) allows to $M_{<001>}$ = 342 GPa and $M_{<100>}$ = 319 GPa. For the <001> direction which is a growth direction of the AlN film the $M_{<001>}$ value is in a very good agreement with the experimental one: $M_{<001>}$ = 340 ± 10 GPa. Note that the effect of the residual stresses on the measured value of the indentation modulus is quite negligible (<1%) as σ_0/H_B< 10% (see appendix A2) [43-45]. Moreover, as soon as the scattering of the measures is concerned, the relative standard deviation $\Delta M/M_{mean}$ is related to the dimensionless parameter R_{ms}/h by the following relation [46-47]:

$$\frac{\Delta M}{M_{mean}} = \alpha \left(\frac{R_{ms}}{h} \right)^{m} \qquad (3)$$

with α = 0.35+-0.1 and m = 0.64. The R_{ms} values have previously been reported in Fig. 2a. Excepted for h = 50 nm, there is a fairly good agreement between the experimental values of the scattering and those given by the relation (3). As an example, for h=100 nm, $\Delta M/M_{mean}$ is in the range 4-6 % over the entire range of Al content. Of course, $\Delta M/M_{mean}$ increases when

the indentation depth decreases and $\Delta M/M_{mean}$ could be greater than 8 % (25-35 GPa) for h = 60 nm which is the indentation depth below which the indentation modulus is independent of the substrate effect ($h/e_f < 2\%$).

The variations of the indentation modulus in the fcc and hcp domains have been connected with the variations of the lattice parameters in these two regions. However, as previously mentioned (section 3.1) and due to the compressive residual stresses the lattice parameters a_i (i= fcc or hcp) calculated from the XRD patterns are overestimated. Knowing the mean value of the residual stress σ_0 (section 4.1), the values of the isotropic indentation modulus and Poisson's ratio, M_{iso} and ν_{iso}, respectively (Table II), the true values a_{i0} of the lattice parameters can be estimated by:

$$a_{i0} = \frac{a_i}{1 - \frac{\sigma_0 \sin^2 \psi}{M_{iso}(1-\nu_{iso})}} \quad , \psi = \pi/2 - \omega \quad \text{and} \quad i = (\text{fcc}) \,\text{or}\, (\text{hcp}) \qquad (4).$$

As an example, for TiN, with $a_{c<100>} = 4.27\,\text{Å}$, σ_0= -2.7 GPa, M_{iso}= 444 GPa, ν_{iso}= 0.2 and ω = 10°, the previous relation gives $a_{c0} = 4.239\,\text{Å}$, which is close to the tabulated value a_{c0}= 4.24 Å. For each composition the a_{c0} values have been calculated.

The indentation modulus increases with the decrease of the lattice parameter, thus:

$$M_{<hkl>}(\text{fcc}) = M_{<hkl>}(\text{TiN})\left(1 - \beta_c \frac{a_{c0} - a_{c0}(\text{TiN})}{a_{c0}(\text{TiN})}\right) \qquad (5a)$$

and a similar expression for the hcp domain:

$$M_{<hkl>}(\text{hcp}) = M_{<hkl>}(\text{AlN})\left(1 - \beta_h \frac{c_{h0} - c_{h0}(\text{AlN})}{c_{h0}(\text{AlN})}\right) \qquad (5b)$$

or with the lattice parameter a_{h0}(AlN) as $\frac{c_{h0}}{a_{h0}} = 1.6 = c^{te}$. β_c and β_h are the two model parameters. For the intermediate compositions the two structures coexist (fcc + hcp) and a simple mixture law has been considered. Hence:

$$M_{<hkl>} = \alpha(x\ \%)\, M_{<hkl>}(fcc) + \left(1 - \alpha(x\ \%)\right) M_{<hkl>}(hcp) \qquad (6a)$$

with $\alpha(x\ \%) = 1$ for $x\ \% < 0.58$ and $\alpha(x\ \%) = 0$ for $x\ \% > 0.7$. The choice of the $\alpha(x\ \%)$ function is somewhat arbitrary and an exponential function which verifies the boundary conditions has been considered. So:

$$\alpha(x\ \%) = \left[\exp - \left(\frac{< x\ \% - 0.58 >}{< 0.7 - x\ \% >} \right) \right]^n \qquad (6b)$$

where $< x > = x\, H(x)$ with $H(x)$ the Heaviside function. The exponent n is a model parameter. The complete model for the evolution of the indentation modulus as a function of the Al content is constituted by Eqs. 5a-b and 6a-b. The identified model with $\beta_c = 1.0$, $\beta_h = 9$, $n = 2$, $M_{iso}(TiN) = 444$ GPa (as <100> and <111> orientations have been observed), $M_{<001>}(AlN) = 342$ GPa, $a_{c0}(TiN) = 4{,}24$ Å and $c_{h0}(AlN) = 4{,}98$ Å has been plotted in Fig. 6b.

Hence, knowing the stiffness coefficients C_{ij} of the TiN and AlN crystals, the preferential growth directions <hkl> of the crystallites and the lattice parameters (a_c, a_h, c_h) determined by XRD, the mean residual stress σ_0 in the film, the indentation modulus values can be estimated thanks to the previous model whatever the x(%Al) content is. Moreover the precise knowledge of the elastic properties of these films is absolutely necessary to correctly identify the plastic coefficients thanks to inverse analysis.

4.2.1.2 Berkovich hardness $H_{B<hkl>}$:

Figure 7a shows the variation of the measured Berkovich hardness $H_{B<hkl>meas}$ as a function of the reduced indentation depth. As for the indentation modulus due to the rounding of the indenter tip the hardness increases with the indentation depth until $h/e_f \sim 4$-5 % [33] and then slightly decreases due to the substrate effect ($H_S = H_B(Si) \sim 13$ GPa $< H_{B<hkl>}$ film). To quantitatively take this effect into account and to determine the true hardness of these films, the Bhattacharya and Nix's model [48] for hard film on softer substrate has been considered. Thus:

$$H_{B<hkl>meas} = H_S + (H_{B<hkl>} - H_S) \exp\left(- \frac{H_{B<hkl>} / H_S}{\sigma_f / \sigma_S \sqrt{E_{<hkl>} / E_S}} \frac{h}{e_f} \right) \qquad (7a)$$

where $H_{B<hkl>}$ and H_S are the hardnesses, σ_f, σ_S the yield strengths, $E_{<hkl>}$, E_S the Young's moduli of the film and the substrate, respectively. In the absence of information on the yield strengths it has been assumed that $H_{B<hkl>}/H_s \sim \delta\ \sigma_f/\sigma_S$ with $0.5 < \delta < 1$. Hence Eq.(7a) is rewritten as:

$$H_{B<hkl>meas} = H_S + (H_{B<hkl>} - H_S)\exp\left(-\frac{1}{\delta\sqrt{E_{<hkl>}/E_S}}\frac{h}{e_f}\right) \qquad (7b)$$

To fit the decreasing of the experimental curves (Fig. 7a) knowing $E_{<hkl>}$, E_S (deduced from the $M_{<hkl>}$ values with $\nu = 0.2$) and H_S ($H_{Si} \sim 13$ GPa) a value of $\delta = 1/2$ has been determined. Thus the yield strength ratio is twice the hardness one. Note that, due to the confinement of the plastic deformation field the decrease of the hardness with the indentation depth is less pronounced than the one of the indentation modulus related to the elastic deformation field (see Fig.8). As a function of the Al content, the measured hardnesses $H_{B<hkl>meas}$ at h = 100, 300 and 600 nm have been reported in Fig. 7b. The extrapolated values for h = 0 correspond to the true hardness of the films. The films deposited on steel substrate (x= 0.5) appreciably present the same hardness as those deposited on Si substrate. As a comparison the results issued from the Kutschej et al. [6] work have also been reported.

The complete analysis of the indentation curves thanks to inverse finite elements modeling is presented in the next section.

5 Inverse finite elements analysis of the indentation curves

5.1 Method

In this section the identification of the plastic material parameters of the films thanks to the different indentation curves is described. The analytical solution for indentation of an elasto-plastic work-hardening solid does not exist [15-22] and the analysis is based on inverse numerical simulation.

The indentation test has therefore been modeled by a 2D axisymmetric representation with the ANSYS finite element software. The semi-vertical angle of the conical indenter $\varphi = 70°3$ gives the same contact area to depth ratio than a perfect Berkovich pyramid [15-22][49]. The cone tip is smoothed by a sphere of radius R (R = 550 nm and 100 nm depending on the used indenter). A film of 3 µm thick on a substrate has been modeled (see Fig.8). Indenter size and

substrate thickness have been determined to be insensitive to far-field boundary conditions: about 40 times greater (~ 25 µm) than the maximum indentation depth (h_{max}~ 600 nm).

The augmented Lagrangian method runs the contact algorithm between the indenter and the film (Coulomb friction coefficient equal to 0.2 **[50]**). In each computation and at the maximum load, the minimum number of contact elements in the contact zone is not less than 16. Note that for this indenter geometry the friction coefficient does not have any influence on the numerical responses **[17][50]**. An implicit method with non-linear geometric formulation has been used with higher order 2D elements. The mesh density has been **refined** in order to the smallest elements are localized in the contact region. A convergence analysis has been performed in order to avoid any mesh influence.

The indenter (E_i = 1100 GPa, ν_i = 0.07) and Si substrate (E_s = 165 GPa, ν_s=0.23, see Table II) have been considered as isotropic linear elastic materials. The case of rigid indenter has also been considered. For the film behavior model and for simplicity an isotropic linear elasto-plastic model has been considered. A very important point: the Young's modulus of the films E(x) is deduced from the $M_{<hkl>}(x)$ experimental indentation modulus values considering a mean Poisson's ratio of ν = 0.21 (Table II). The considered loading surface is:

$$f = \bar{\sigma}_{VM} - R_s - \sigma_y \quad \text{with} \quad dR_s = H_p^* \, \overline{d\varepsilon_p} \tag{8}.$$

$\bar{\sigma}_{VM}$ and $\overline{d\varepsilon_p}$ are the von Mises stress and the equivalent von Mises plastic strain increment, R_s the radius of the loading surface (isotropic hardening variable), σ_Y the yield stress and H_p^* the linear hardening coefficient. Note that the isotropic elastic behavior of the films is perfectly justified for fcc phase but less for the hcp phase. Hence, as the Young's moduli and the Poisson ratio are known, the two only unknowns of the model are the yield stress σ_Y and the linear hardening coefficient H_P^*.

It is well known that indentation methodologies suffer from the non-uniqueness and sensitivity of the determined material properties [18-24][51-53]. It has been shown that the phenomena are not independent, rather non-uniqueness is an extreme case of sensitivity [24]. In this work, the quality of the estimations is evaluated through an identifiability index and it has been shown that the use of a non-rigid indenter in the model and tip rounding improve the sensitivity of the determined material parameters.

To identify the optimal set of parameters $\hat{\boldsymbol{\theta}} = (\hat{\theta}_1, \hat{\theta}_2) = (\sigma_Y, H_P^*)$, an inverse method has been used. The details of the procedure (Eq.A3-1), the method to calculate the uncertainties (Eq.A3-4) and the quantification of the quality of the estimations thanks to an identifiability index $\hat{\mathfrak{I}}(\hat{\boldsymbol{\theta}})$ (Eq.A3-5) are given in Appendix A3.

5.2 Results

All sets of randomly chosen initial input parameters $\boldsymbol{\theta}_0$ calculated by the genetic global algorithm using the loading curve lead to the same $\hat{\boldsymbol{\theta}}$ solution determined by the local algorithm [54]. Hence, the numerical uniqueness is considered as guaranteed. Whatever the Al content (for R = 550 nm and 100 nm) the practical identifiability analysis shows that the mean value of the identifiability index $\hat{\mathfrak{I}}(\hat{\boldsymbol{\theta}})$ does not decrease during the unloading part of the indentation curves. Therefore the unloading part of the curves is not necessary as the Young's moduli of the films are known. On the contrary, the mean value of $\hat{\mathfrak{I}}(\hat{\boldsymbol{\theta}})$ greatly depends on the tip radius, $\mathfrak{I}(R = 550\text{nm}) = 1.9$ and $\mathfrak{I}(R = 100\text{nm}) = 2.6$ (critical identifiability).

In order to illustrate the tip rounding, the deformability of the indenter and the substrate effects on identifiability, the following tests have been performed. $\mathfrak{I}$ has been calculated for x = 0.5 with R=500 nm, but also for three virtual cases: sharp and blunt indenters, rigid and elastic indenter associated with bulk and thin specimen (film thickness = 40 h_{max}). Table III shows that the identifiability is significantly improved when compared with sharp indenter (12%), rigid indenter (24%), but that for the considered thickness the substrate effect does not affect the index. So, the elasticity effect and the tip radius of the Berkovich indenter are shown to be two very relevant parameters to correctly identify the plastic parameters of the behavior law.

Complete identification procedure for the set of Al contents has been conducted for rigid and elastic indenters. Figures 8 and 9 give, for a deformable indenter, examples of elastic and plastic von Mises strain fields (x=0.5) and of the fit of the loading experimental curves by the numerical model (x= 0, 0.5, 0.86 and1), respectively. The elastic deformation of the indenter on one hand and the substrate and the confinement of the plastic deformation for the maximum loading (P_{max}=160 mN) on the other hand are clearly highlighted in Fig.8.

Simulation results (examples in Fig.9) show a very good agreement with the experimental results, excepted at x = 0 and x = 1 where a fairly good agreement is obtained (see the errors in Table IV), probably due to local cracking in these less ductile materials. Figure 10 shows, as a function of the Al content and for rigid and deformable indenters, the evolution of the optimal values of σ_Y and H_P^*. For the legibility of the Fig.10 the uncertainties $\hat{\boldsymbol{\Delta\theta}}$ calculated using Eqs.(A3-1 and 4) (elastic indenter) determined from the experimental loading curves and corresponding to the tests carried out with R = 550 nm and 100 nm are given in Table IV. Note that no value of these two parameters are reported in the literature. The yield stresses σ_Y and the hardening coefficients H_P^* lie in the range 4.2 to 6.8 GPa and 60 to 400 GPa, respectively. With R = 550 nm, the mean value of the relative uncertainty on the yield stresses calculated using Eq.(A3-4) is about $\Delta\sigma_Y / \sigma_Y \approx 40\%$ ($16\% < \Delta\sigma_Y / \sigma_Y < 71\%$) and the relative uncertainty on the hardening coefficient is approximately 1.7 times greater: $\Delta H_P^* / H_P^* \approx 70\%$ ($25\% < \Delta H_P^* / H_P^* < 150\%$). However, with R = 100 nm and x=0.6, $\Delta\sigma_Y / \sigma_Y \approx 90\%$ and $\Delta H_P^* / H_P^* \approx 300\%$ which corresponds to a great loss of identifiability (see Table III for the $\hat{\Im}(\boldsymbol{\theta})$ index with a sharp indenter). **Such high uncertainties in the determined material parameters have been reported by previous researchers [24][51-53].** Although the identified curves perfectly match the experimental ones (see the errors in table IV), the uncertainties on the plastic coefficients are relatively large as they are linked to the low convexity of the function to minimize.

For rigid indenter the values of σ_Y and H_P^* have also been reported in Fig.10. The σ_Y values are appreciably independent of the indenter stiffness, contrary to the H_P^* values which are about 3 to 4 times lower than those calculated with an elastic indenter. However, their evolutions with the Al content are quite similar. These different points are discussed in the following section.

5.3 About the relationship between plastic parameters, hardness and rigidity of the indenter:

Considering the generalized Tabor's relation [55], the corresponding stress $\sigma_{(\Delta\varepsilon pm)}$ should be equal to:

$$\sigma_{(\Delta\varepsilon pm)} = \sigma_Y + H_p^* \, \Delta\varepsilon_{pm} = H_{B0}/3 \quad (9)$$

where H_{B0} is the true hardness at zero stress (see appendix A2-1). If the indenter is rigid and the Berkovich tip perfect, the representative point of the stress-strain curve determined by inverse method should be at $\Delta\varepsilon_{pm}$ = 3.3 % [15-18]. However, due to the tip rounding and the indenter stiffness, the representative point evolves with these two parameters [16] [55]. To approximately determine the mean value of the representative strain $\Delta\varepsilon_{pm}$ for the used blunt Berkovich tip (R=550 nm), a perfect correlation between the Tabor's stress and the flow rule is argued (Eq.9). Knowing σ_Y, H_P^* and H_{B0} for the set of composition, mean values of $\Delta\varepsilon_{pm}$ ~ 4.2 ± 0.5% and 1.1 ± 0.2% have been obtained for rigid and elastic indenters, respectively. Note that the first value is in the range 3.3 % to 6.8 % corresponding to a perfect Berkovich tip and a spherical cap at the tangent point to the conical shape ($\Delta\varepsilon_P \approx 0.2\sqrt{2h/R}$), respectively. For the two considered cases, as σ_Y is practically independent of the indenter stiffness, the ratio ~3.8 between the two representative strains is approximately equal to the ratio between the hardening coefficients (~3 to 4).

For these very hard coating films, the elasticity of the diamond of the indenter greatly affects the values of the hardening coefficients H_P^* determined by inverse analysis and the representative plastic strain for our blunt Berkovich tip is about 1%, thus three to four times lower than the expected one for a perfect rigid tip.

6 – Discussion and analysis with regards to the literature

An interesting result which has never been directly evidenced is illustrated in Fig. 11 with the H_P^*/σ_Y ratio, is the capacity as a function of the Al content of the film to exhibit plastic strain hardening. This ratio is maximum for x= 0.5 and 0.6: $H_P^*/\sigma_Y \approx 60-70$. The same tendency has been obtained with a rigid indenter but in a ratio of 3-4 (Fig.11). Indeed, this observation should be linked to the film toughness. The toughness of 3 µm thick films deposited on steel substrate by the same sputtering procedure as the one of the present study have recently been reported by Henry et al. [56]. On these films, the "Scratch Crack Propagation Resistance" (CPRs) criterion proposed by Zhang et al. [57] has been evaluated

and the values reported in Fig.11. H_P^* / σ_Y and CPRs follow similar evolutions. Contrary to the Al rich films which present a weak resistance to the crack initiation, particularly for the AlN, the films with fcc structure exhibit a better fracture toughness. Note that the same conclusion could be obtained from the fracture toughness K_{1c} evaluated thanks to radial crack length measurements after Vickers indentations [56][58-59]. TEM studies [12] on cross-section of TiN milled by focused ion beam revealed that the microstructure of TiN is made of small grains clustered in vertical columns whereas Al rich films like for x = 0.86 consists of long fibers well textured along the <002> direction of hexagonal structure. Hence, the propagation of cracks within the film is thus easier along fibers in hcp domain whereas it is better impeded by a structure composed of small grains like in fcc region. The aptitude of the films to support plastic deformation follows the variation of the toughness.

Concerning the indentation modulus M and the hardness H, the presented results are close to those reported by Kutschej et al. [6] for dc magnetron sputtered films at relatively low temperature (T_d~350°C) and agree with those of Hörling et al. [7] after an annealing at 1050°C of the as deposited film to suppress the stress build-up created during the film deposition by the lattice point defects. The critical composition of the sharp decreasing of the mechanical properties is located in the 0.62 to 0.69 range (Kutschej et al. [6]: 0.67 - 0.69, Hörling et al. [7]: 0.66 - 0.67 and the present study: 0.62 - 0.66) and are in a fairly good agreement with the theoretical one [2]: $x = 0.65 \pm 0.05$.

7 – Conclusions

The mechanical properties of $Ti_{1-x}Al_xN$ ($0 < x < 1$) films of different thickness deposited by r.f. reactive magnetron sputtering on Si <100 > and high speed steel substrates have been investigated. The coatings with x < 0.58-0.59 present cubic structure whereas for x > 0.7 a hexagonal structure is observed. Between these two limits the two structures coexist. The cubic structure shows a $(200)_c$ and $(111)_c$ preferred crystallization orientation whereas $a(002)_h$ orientation is observed for the hcp structures. The roughness and the superficial mean column diameters ϕ depend on the Al content and on the film thicknesses. A minimum is observed in the vicinity of x = 0.6. ϕ is in the 60-120 nm range whereas the crystallite diameters d* estimated by XRD and AFM are in the range 7 to 35 nm. As soon as small amount of hcp structure appears the resistivity sharply increases. Excepted for the AlN coating the residual

stresses are compressive. As for the other measured properties the residual stress presents a minimum at the neighborhood of x~0.64.

The indentation modulus $M_{<hkl>}$ and the Berkovich hardness $H_{B<hkl>}$ values greatly depend on the composition and a transition occurs when the two structures coexist for $0.58 < x < 0.7$. To describe the $M_{<hkl>} = f(x\ \%)$ evolution a simple model taking into account the C_{ij} stiffnesses of TiN and AlN, the variations of the lattice parameters with the composition and the residual stresses, and the preferred crystallite orientations has been proposed.

Inverse finite elements analysis of the indentation curves considering the tip rounding, the elasticity of the indenter and a simple isotropic linear elasto-plastic law whose elastic parameters are known (Young's modulus and Poisson's ratio) allows the yield stress σ_Y and the hardening coefficient H_p^* to be extracted: σ_Y and H_p^* lie in the ranges 4.2 to 6.8 GPa and 60 to 400 GPa, respectively. **However, due to the low convexity of the functions to minimize, for a tip radius close to 500 nm the uncertainties on these two parameters are of the order of 40 to 70%, but drastically increase (up to 200 to 400%) for very sharp indenter (R~100 nm).** Moreover, due to the great hardness of these films and the elasticity of the diamond of the indenter, the representative plastic strain is obtained at about 1.1% thus three times lower than the expected one. The maximum value of H_p^* / σ_Y which characterizes the ability of these films to exhibit plastic strain is obtained in the fcc domain and fcc domain with a small amount of hcp phase, for x = 0.5 and 0.6. The quality of the estimations was discussed through a practical identifiability study and it has been shown that tip rounding and elasticity of the indenter offer informations which combined themselves improve the identifiability (+24%).

As the conclusion and according to the different published works on the mechanical properties of these ternary coatings, the optimum properties are located in the 0.5 to 0.6 composition range.

Appendix A1

In nano-indentation procedure, the $M_{<hkl>}$ modulus measured on a single crystal (or on a well textured material with very fine grains) whose normal to the surface has director cosine α_i is given by [60][61]:

$$M_{<hkl>} = 16\pi^2 \left[\int_0^{2\pi} \alpha_m \, \beta_{km}^{-1} \left[C_{ij}(\gamma) \right] \alpha_k \, d\gamma \right]^{-1} \quad \text{with}$$

$$M_{<hkl>} = \left[\frac{1}{M_r} - \left(\frac{1-\nu^2}{E} \right)_{ind} \right]^{-1} \quad \text{and} \quad M_r = \frac{\sqrt{\pi}}{2\beta\sqrt{A_c}} \frac{dP}{dh} \qquad \text{(A1-1a)}$$

For a Berkovich indenter the projected contact area A_c is given by:

$$A_c(h_c) = 24{,}56\, h_c^2 + \sum_{n=1}^{4} (a_n h_c^{1/n}) \quad \text{with} \quad h_c = h - \varepsilon \frac{P}{S} \qquad \text{(A1-1b)}$$

In these relations P is the applied load, S = dP/dh the unloading stiffness measured at the depth of penetration h, $\beta = 1.034$ and $\varepsilon = 0.72$ for the Berkovich'tip [19]. $(E/(1-\nu^2))_{ind}$ is the reduced modulus of the diamond indenter. γ is the angle in surface plane and β_{mk} a very complicated matrix functions of the elastic stiffnesses $C_{ij}(\gamma)$ [60][61]. No general exact analytic solution of Eq.(A1-1a) exists. Nevertheless, for solids with cubic symmetry, Vlassak and Nix [60] showed that, using a numerical modeling, the following equations can be written:

$$M_{<hkl>} = \beta_{<hkl>} \left(\frac{E}{1-\nu^2} \right)_{iso} \quad \text{with} \quad \beta_{<hkl>} = a + c\,(f_{ani} - f_o)^n \quad \text{and} \quad f_{ani} = \frac{2C_{44}}{C_{11} - C_{12}} \qquad \text{(A1-2)}$$

$(E/1-\nu^2)_{iso}$ is the isotropic reduced modulus calculated thanks to the Hashin and Shtrickman [40] relations for homogenized materials. Coefficients a, c, f_o and n depend on the Poisson ratio $\nu_{<100>}$ and on the crystal orientation <hkl>. f_{ani} is the anisotropic coefficient. Note that for

isotropic materials, $f_{ani} = 1$ which makes $\beta_{<hkl>} = 1$ and, as a result, $M_{<hkl>} = \left(\frac{E}{1-\nu^2}\right)_{iso}$. This formulation is usually used in the literature and Eq.(A1-1a) is recasted as:

$$\left(\frac{E}{1-\nu^2}\right)_{iso} = \left[\frac{1}{M_r} - \left(\frac{1-\nu^2}{E}\right)_{ind}\right]^{-1} \tag{A1-3}$$

For orthotropic materials, good analytical approximated solutions are given by Delafargue and Ulm [62]. Hence, for the hexagonal structure the indentation moduli in the <001>, <110> and <100> directions are written as:

$$M_{<001>} = \frac{2}{\sqrt{\frac{C_{11}}{C_{11}C_{33} - C_{13}^2}\left(\frac{1}{C_{44}} + \frac{2}{\sqrt{C_{11}C_{33}} + C_{13}}\right)}} \quad \text{and}$$
$$M_{<100>} = M_{<110>} = \sqrt{\frac{C_{11}^2 - C_{12}^2}{C_{11}}\sqrt{\frac{C_{11}}{C_{33}}}}\, M_{<001>} \tag{A1-4}$$

Based on the works of Delafargue and Ulm [62] and for cubic and hexagonal structures, Delobelle et al. [41] have proposed a general approximated solution applicable whatever the orientation is. Hence,

$$M_{<hkl>} = M_{iso}\sqrt{\frac{< C_{11}^* >}{< C_{33}^* >}} \quad \text{with} \quad < C_{ij}^* > = \frac{1}{2\pi}\int_0^{2\pi} \alpha_m \left[C_{ij}(\gamma)\right]_{mk} \alpha_k \, d\gamma \tag{A1-5}$$

As for the Eq.(A1-2) $M_{iso} = (E\text{-}1/\nu^2)_{iso}$ is the isotropic reduced modulus and $< C_{ij}^* >$ represent the mean values in the indentation plane (integration following the γ angle) of the elastic stiffnesses written in the indentation direction.

TiN is weakly anisotropic [37] and the C_{ij} values taken into account [38-39] are listed in Table II. The values of M_{iso} and ν_{iso} evaluated thanks to the Hashin and Shtrickman formulation [40] have also been reported in Table II. Applying the Eq.(A1-5) for the growth directions of the TiN film with:

$$< C_{11}^{*} > = C_{11} \quad \text{and} \quad < C_{33}^{*} > = \frac{3C_{11} + C_{12} + 2C_{44}}{4} \quad \text{for the} < 100 > \text{direction}$$
$$< C_{11}^{*} > = \frac{C_{11} + 2C_{12} + 4C_{44}}{3} \text{ and } < C_{33}^{*} > = \frac{C_{11} + C_{12} + 2C_{44}}{2} \text{ for the} < 111 > \text{direction} \qquad \text{(A1-6)}$$

the values of $M_{<100>}$ = 450 GPa and $M_{<111>}$ = 440 GPa are obtained. The application of the Vlassak et al. model [60] (Eq.A1-2) appreciably gives the same values.

For the AlN, the C_{ij} coefficients of sputtered thin films [42] are listed in Table II. As previously done, the application of Eq.(A1-5) with:

$$< C_{11}^{*} > = C_{33} \quad \text{and} \quad < C_{33}^{*} > = C_{11} \quad \text{for the} < 001 > \text{direction}$$
$$< C_{11}^{*} > = C_{11} \quad \text{and} < C_{33}^{*} > = \frac{3C_{11} + 2C_{13} + 3C_{33} + 4C_{44}}{8} \quad \text{for the} < 100 > \text{direction} \qquad \text{(A1-7)}$$

and M_{iso} =304 GPa allows to $M_{<001>}$ = 342 GPa and $M_{<100>}$ = 319 GPa. The application of the Delafargue and Ulm's model [62] (Eq. A1-4) appreciably gives the same values.

Appendix A2

As shown by different authors [43-45] the measured values of the hardness H_B and of the indentation modulus M depend on the level of the residual stress beneath the indented surface. To take this effect into account the relation (A2-1) and which has been verified by F.E. analysis [45] has been proposed by Suresh et al. [34]:

$$H_B = H_{B0}\, f\left(\frac{\sigma_o}{H_{B0}}\right) \quad \text{with :} \quad f\left(\frac{\sigma_o}{H_{B0}}\right) = \left(1 + \frac{\sigma_o}{H_{B0}}\right)^{-1} \quad \text{if} \quad \sigma_0 > 0$$
$$f\left(\frac{\sigma_o}{H_{B0}}\right) = \left(1 - \frac{|\,\sigma_0\,|\sin\alpha}{H_{B0}}\right)^{-1} \quad \text{if} \quad \sigma_0 < 0 \qquad \text{(A2-1)}$$

H_{B0} is the true hardness at zero stress and $\alpha = (\pi - \varphi)/2$ where φ is the vertical angle of the conical tip. Solving the relations (A2-1) knowing H_B and σ_0 the H_{B0} values can be calculated. The same kind of relation can be deduced for the influence of the residual stress on the indentation modulus:

$$M = M_0 \sqrt{f\left(\frac{\sigma_0}{H_{B0}}\right)} \quad \text{where} \quad f\left(\frac{\sigma_0}{H_{B0}}\right) \ \text{is given in} \ (A2-1) \qquad (A2-2).$$

In these two expressions the σ_0/H_{B0} ratio is the argument of the f function. In this study due to the small values of this argument ($\sigma_0/H_{B0} < 10\%$) the corrections on the indentation modulus and the hardness are appreciably negligible (<2%).

Appendix A3

To identify the optimal set of parameters $\hat{\boldsymbol{\theta}} = (\hat{\theta}_1, \hat{\theta}_2) = (\sigma_Y, H_P^*)$, an inverse method is used. The experimental indentation curves are discretized in time by a sequence of M discrete instants t_k (≈ 20 instants). At each step k, the indentation load P_{ck} (subscript c for calculated) corresponding to the experimental indentation depth $h(t_k)$ is calculated using the numerical model of the behavior's law (Eq.8). The minimization problem formulated by the Eq.A3-1 consists in the minimization of an objective function $\omega(\theta_1, \theta_2)$ which quantifies the overall discrepancy between the measured quantities P_{ck} and the corresponding computed values $P_{ck}(\theta_1, \theta_2)$ [54]:

$$\begin{cases} \hat{\boldsymbol{\theta}} = \arg\min_{\boldsymbol{\theta} \in [\boldsymbol{\theta}^-, \boldsymbol{\theta}^+]} \omega(\boldsymbol{\theta}) \\ \omega(\boldsymbol{\theta}) = \dfrac{1}{2M} \displaystyle\sum_{k=1}^{M} \left[\frac{P_{ck}(\boldsymbol{\theta}) - P_k}{P_{\max}} \right]^2 \end{cases} \qquad (A3\text{-}1).$$

P_{max} is the maximum indentation load which makes ω dimensionless. $\boldsymbol{\theta}^-$ and $\boldsymbol{\theta}^+$ are the minimum and maximum values of the parameters.

The constrained minimization process combines a global (genetic algorithm) [63][64] and a local (Levenberg-Marquard algorithm) [65][66] algorithms implemented in a Matlab toolbox MIC2M (mic2m.univ-fcomte.fr). An exploration of the field ($\theta_1 = [0,10]\text{GPa}, \theta_2 = [0,500]\text{GPa}$) is performed using the global genetic algorithm to find different sets of initial input parameters $\boldsymbol{\theta}_0$ required in the local algorithm. Hence, the numerical uniqueness is considered as guaranteed if all of these $\boldsymbol{\theta}_0$ parameters lead to the same solution $\hat{\boldsymbol{\theta}}$ using the local algorithm. The determination of the uncertainty $\boldsymbol{\Delta}\hat{\boldsymbol{\theta}}$ of the

identified parameters $\hat{\boldsymbol{\theta}}$ is based on the quadratic approximation (used in the local algorithm) of the objective function ω around $\hat{\boldsymbol{\theta}}$:

$$\omega(\Delta\hat{\boldsymbol{\theta}}) \approx \tilde{\omega}(\Delta\hat{\boldsymbol{\theta}}) = \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}\Delta\hat{\theta}_i\Delta\hat{\theta}_j \left.\frac{\partial^2\omega}{\partial\theta_i\partial\theta_j}\right|_{\hat{\boldsymbol{\theta}}} = \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{\Delta\hat{\theta}_i\Delta\hat{\theta}_j}{\hat{\theta}_i\hat{\theta}_j}\overline{H}_{ij}(\hat{\boldsymbol{\theta}}) \qquad \text{(A3-2).}$$

$\bar{\mathrm{H}}(\hat{\boldsymbol{\theta}})$ is the 2x2 rescaled Hessian matrix which can be approximated by Eq.A3-3 and computed by finite difference method.

$$\overline{H}_{ij}(\hat{\boldsymbol{\theta}}) = \hat{\theta}_i\hat{\theta}_j \left.\frac{\partial^2\omega}{\partial\theta_i\partial\theta_j}\right|_{\hat{\boldsymbol{\theta}}} \approx \frac{1}{M}\frac{\hat{\theta}_i\hat{\theta}_j}{P_{\max}^2}\sum_{k=1}^{M}\left[\left.\frac{\partial P_{ck}(\boldsymbol{\theta})}{\partial\theta_i}\right|_{\hat{\boldsymbol{\theta}}}\left.\frac{\partial P_{ck}(\boldsymbol{\theta})}{\partial\theta_j}\right|_{\hat{\boldsymbol{\theta}}}\right] \quad (i,j=1,2) \qquad \text{(A3-3).}$$

Parameters uncertainties can then be approximated using the inverse matrix $\bar{\mathrm{V}}(\hat{\boldsymbol{\theta}}) = \bar{\mathrm{H}}_{\mathrm{ij}}(\hat{\boldsymbol{\theta}})^{-1}$ in the following relations:

$$\frac{\Delta\hat{\theta}_i}{\hat{\theta}_i} \approx \sqrt{2\omega(\hat{\boldsymbol{\theta}})\overline{V}_{ii}(\hat{\boldsymbol{\theta}})} \quad (i,j=1,2) \qquad \text{(A3-4).}$$

The sensibility of the results to the different geometrical parameters of the F.E. model (tip rounding, elasticity of the indenter and substrate effects) and to the data considered on the experimental indentation curve can be evaluated by examining a scalar parameter $\Im(\hat{\boldsymbol{\theta}})$ which quantify the identifiability improvement [67][68]. Indeed, the $\bar{\mathrm{H}}$ matrix in Eq.(A3-3) can be badly conditioned and the computation of its inverse is prone to large numerical errors (poor identifiability). It can be evaluated through a local identifiability index:

$$\Im(\hat{\boldsymbol{\theta}}) = \log_{10}\left[\frac{\lambda_{\max}}{\lambda_{\min}}\right] \qquad \text{(A3-5).}$$

λ_{max} and λ_{min} are the highest and the smallest eigen-values of the $\bar{H}(\hat{\boldsymbol{\theta}})$ matrix, respectively. If $\mathfrak{I}(\hat{\boldsymbol{\theta}})$ is close to 0, the matrix is well conditioned which means its inverse can be computed with very good accuracy. At the opposite, if $\mathfrak{I}(\hat{\boldsymbol{\theta}})$ is large the matrix is considered as poorly conditioned. In the literature and in the different fields of sciences some values about suitable limits are available: $\mathfrak{I}(\hat{\boldsymbol{\theta}}) < 2$: good identifiability and $\mathfrak{I}(\hat{\boldsymbol{\theta}}) > 3$: poor identifiability [69]. For a value between 2 and 3, acceptability depends on the expected accuracy of the results. Considering the indentation analysis a 2.5 value appears to be a critical threshold below which the identification can be considered as acceptable [25]. Nevertheless, whatever the critical threshold, the variations of $\mathfrak{I}(\hat{\boldsymbol{\theta}})$ can be studied to quantify the effects of the geometrical parameters of the F.E. model on the identifiability improvements due to the tip rounding, the elasticity of the indenter, the substrate effect and the data used on the indentation curve (loading/unloading parts). An example is given in the 5.2 section of the text.

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Figure captions

Fig. 1: Lattice parameters determined by XRD as a function of the Al content. Determination of the structural domains: fcc (a_c< 200> and a_c<111>), hcp (a_h<002>, c_h<002>) and fcc + hcp (a_c< 200>, a_h<002>, c_h<002>).

Fig. 2: a)- Roughness R_{ms} as a function of the Al content for different scan areas (4 x 4 μm^2, 1 x 1 μm^2 and 0.25 x 0.25 μm^2) and two films thicknesses (e_f ~ 1 µm and 3 µm). b- Mean diameters ϕ of the top of the columns and mean diameters d* of the crystallites deduced from the AFM and SEM pictures and the FWMH of the XRD patterns.

Fig. 3: Electrical resistivity as a function of the Al content.

Fig. 4: Deflection δ_m as a function of the square length L^2 of the cantilevers for each elaborated materials.

Fig. 5: Calculated residual stresses σ_o as a function of the Al content. Results obtained in previous unpublished work (sputtering at T_d = 350°C) have also been reported.

Fig. 6: a)- Evolution of the measured indentation modulus $M_{<hkl>}$ as a function of the reduced depth h/e_f for the different studied films. Modeling with the King's relation Eq.(2).

b)- Indentation modulus $M_{<hkl>}$ of the different tested films. Modeling thanks to the Eqs.(5-6). The Kutschej et al. [6] results have also been reported.

Fig. 7: a)- Berkovich hardness $H_{B<hkl>}$ for the different tested films as a function of the reduced depth h/e_f. Modeling with the Bhattacharya's relation Eq.(7b).

b)- Hardness as a function of the Al content for three indentation depths (h=100, 300 and 600 nm). Modeling with the Battacharya's equation and determination of the true hardness $H_{B<hkl>}$ at h = 0. The results obtained with a steel substrate and those of Kutschej et al. [6] have also been reported.

Fig 8: Example of elastic and plastic von Mises strain fields for R=550 nm, P_{max}=160 mN and x= 0.5.

Fig 9: Examples of experimental and calculated curves thanks to inverse method for x= 0, 0.5, 0.68 and 1.

Fig. 10: Yield stress σ_Y and linear hardening coefficient H_P^* determined thanks to inverse finite elements analysis as a function of the Al content. Cases of rigid and elastic

indenters. Two equivalent cones corresponding to the two utilized Berkovich tips (R = 550 nm and 100 nm) have been considered.

Fig. 11: Plastic strain indicator H_p^*/σ_Y identified in the cases of rigid and elastic indenters as a function of the Al content. Confrontation to the CPRs criterion values.

Table I

				Thickness of the films e_f(nm)			
				Si<100> substrate		Steel substrate	
Composition	X(Al%)	$S_{Al}/(S_{Al}+S_{Ti})$	V_d (nmh^{-1})	XRD	Stress AFM	Nanoind AFM.	Nanoind.
Ti N	0	0	213	210	613	~3000±100	-
$Ti_{0.62}Al_{0.38}N$	0.38	0.17	248	260	992	~3000±100	-
$Ti_{0.5}Al_{0.5}N$	0.5	0.25	344	245	1012	~3000±100	~3000
$Ti_{0.4}Al_{0.6}N$	0.6	0.33	380	380	1007	~3000±100	~2000
$Ti_{0.32}Al_{0.68}N$	0.68	0.42	405	320	1565	~3000±100	-
$Ti_{0.14}Al_{086}N$	0.86	0.67	522	270	1850	~3000±100	-
Al N	1	1	670	310	1582	~3000±100	-

Table I: Composition, deposition rate and thicknesses of the studied films

Table II

	TiN (fcc)	Si (fcc)	AlN (hcp)	
C_{ij} (GPa)	C_{11} = 498, C_{12} = 106, C_{44} = 168 [38] C_{11} = 507, C_{12} = 96, C_{44} = 163 [39]	C_{11} = 165.7, C_{12} = 63.9, C_{44} = 79.6	-	C_{11} = 360, C_{13} = 123, C_{33} = 410, C_{44} = 116, C_{66} = 119 [42]
f_{ani}	0.854 [38] 0.794 [39]	1.56	-	-
M_{iso}, ν_{iso}	444 , 0.197 [38] 447 , 0.203 [39]	172.8 , 0.23	M_{iso} (GPa)	304
$M_{<100>}$ (GPa)	450 [38] 456 [39]	166	$M_{<001>}$ (GPa)	342
$M_{<111>}$ (GPa)	439 [38] 440 [39]	177	$M_{<100>}$ (GPa)	319

Table II: Stiffnesses C_{ij} and indentation moduli $M_{<hkl>}$

Table III

	Present study	**Virtual 1**	**Virtual 2**	**Virtual 3**	**Virtual 4**
Tip rounding (R=550 nm)	YES	YES	YES	NO (sharp)	NO (sharp)
Film thickness (3 µm)	YES	NO (bulk)	YES	YES	NO (bulk)
Deformable indenter	YES	YES	NO (rigid)	YES	NO (rigid)
$\hat{\Im}(\theta)$ (loading)	1.7 (reference)	1.7 0%	2.1 +24%	1.9 +12%	2.0 +18%

Table III: Tip rounding, deformable indenter and substrate effects on the identifiability index $\hat{\Im}(\theta)$ for x=0.5. The reference is the column present study

Table IV

x (%)Al	R (nm)	E (GPa)	σ_Y (GPa)	H_p^* (GPa)	Error: ω Eq.A3.1	$\Im$(load) Eq.A3.5	$\Delta\sigma_Y/\sigma_Y$ (%)	$\Delta H_p/H_p$ (%)
0	550	366	6.4	113	1.3E-4	1.9	71	150
0.38	550	403	6.6	318	1.8E-5	1.6	32	41
0.5	550	417	5.7	405	8.1E-6	1.7	30	25
0.68	550	248	5.9	97	7.6E-6	2	16	32
0.86	550	328	5.1	151	1.1E-5	2.1	45	43
1	550	319	6.74	65	6.9E-5	2.3	47	122
mean value(R=550 nm)	-	-	~6.1	-	-	~1.9	~40	~69
0	100	366	9.4	46	5.7E-4	2.4	93	380
0.6	100	342	4.2	277	1E-4	2.7	320	280
mean value(R=100 nm)	-	-	~6.8	-	-	~2.5	~210	~330

Table IV: Identified values of the plastic parameters σ_Y and H_p^*, quadratic error $\hat{\omega}(\theta)$ on the fit, $\Im$(load) index value and uncertainties of the identified values $\Delta\sigma_Y/\sigma_Y$, $\Delta H_p/H_p$